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The Fischer-Tropsch and Related Syntheses

Including a Summary of Theoretical and Applied Contact Catalysis

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Foreword

The investigations on which this book are based are part of the Synthetic Liquid Fuels program carried out under public laws 290 (78th Congress) and 443 (80th Congress). The authors are staff members of the Research and Development Branch of the Office of Synthetic Liquid Fuels. The book is published by permission of the Director, Bureau of Mines.

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Preface

Early in 1945 inspection of German plants and interrogation of German engineers and scientists were made possible by the advance of the Allied armies into Germany. Before the fighting in World War II had ceased, British and American teams of technical men from the fuel and chemical industries, and from academic, industrial, and government research laboratories were organized and sent to Germany. Selected documents from the files of many German plants and research laboratories were sent to London, where they were photographed on microfilms, copies of which were sent to the United States. Here a committee from the Petroleum Administration for War and later the Bureau of Mines and the Office of Publications Board of the Department of Commerce prepared indexes of the information contained in the microfilm reels, and made copies of both of these available to United States citizens. A few of the most important documents were translated by the Bureau of Mines and oil company research personnel. Later the Technical Advisory Committee of the Petroleum Administration for War arranged for additional translations to be published by Charles A. Meyer and Co., Inc., 52 Vanderbilt Ave., New York, N. Y. Reports on the inspection of German plants and laboratories and on the interrogation of German engineers and scientists were written by members of the British and American teams. These reports were published by the C.I.O.S. (Combined Intelligence Objectives Subcommittee), F.I.A.T. (Field Intelligence Agency, Technical), and O.P.B. (Office of Publications Board) in the United States, and the B.I.O.S. (British Intelligence Objectives Subcommittee) in Great Britain. In 1946–1948, special summary reports were written by outstanding German technologists under the direction of Dr. W. E. Faragher of the Houdry Process Company, in his capacity as a consultant for the U. S. Bureau of Mines.

This book is the result of an extensive and critical review of the large number of reports and documents pertaining to the selective catalytic hydrogenation of carbon monoxide, or the Fischer-Tropsch and related syntheses, for the production of aliphatic hydrocarbons and alcohols. It is a summary of the work of many chemists and engineers employed by the U. S. Bureau of Mines in the synthetic liquid fuels office and by the

British Fuel Research Laboratory; of special consultants from the oil, coal, and gas industries of the United States; and of German scientists and engineers. The last mentioned were employed to supply "background" information without which many of the data in captured German documents could not have been satisfactorily evaluated. British scientists and engineers collaborated in collecting and interpreting German documents and interrogating a large number of German technologists.

Although three chapters of the manuscript are devoted to the more fundamental scientific aspects of the hydrogenation of carbon monoxide, the major portion of the book is concerned with detailed discussion of the development of the Fischer-Tropsch and related processes. Sufficient original data have been included to permit the reader to make his own evaluations and correlations of experimental results. To further assist the reader in evaluation of the original data, the references given in the book to sources of information include citations of virtually all important published documents, but no attempt is made to provide an exhaustive survey. The sections on heterogeneous catalysis and on kinetics and reaction mechanisms are based largely on the work of P. H. Emmett and his collaborators. These sections and the one on thermodynamics of hydrogenation of carbon monoxide are highly condensed and somewhat "heavy" reading for those interested mainly in industrial process design, but because they contain theoretical background information and a summary of the present-day fundamental knowledge of the synthesis these sections should be regarded as essential reading for those engaged in research and development work on hydrogen-carbon monoxide reactions.

Although the number of technologists on whose work the book is based is too large for individual mention, it is desirable to list those whose efforts were of major importance. In the latter group were M. A. Elliott, L. L. Newman, W. C. Schroeder, A. C. Fieldner, J. Wiley, L. L. Hirst, and Miss H. Anderson of the U. S. Bureau of Mines, H. V. Atwell of The Texas Company, W. E. Faragher of the Houdry Process Corporation, A. E. Miller of the Sinclair Oil Company, C. C. Hall of the British Fuel Research Laboratory, R. Holroyd of Imperial Chemical Industries, Ltd., L. Alberts, formerly with Ruhrchemie, and H. Pichler, formerly with the Kaiser Wilhelm Institute for Coal Research. The first draft of the manuscript was reviewed and constructive criticisms were made by L. J. E. Hofer, J. F. Shultz, W. K. Hall, J. Field, B. Seligman, H. Benson, S. Weller, R. Kelly, M. Orchin, I. Wender, J. H. Crowell, D. Bienstock, and M. Festenstein of the Bureau of Mines. Professor W. Edmister of Carnegie Institute of Technology reviewed the section on thermodynamics. Special mention is desirable also for the following Bureau of Mines per-

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Structure and Reactivity of Hydrogen, Carbon Monoxide, Iron, Cobalt, and Nickel and the Thermodynamics of the Hydrogenation of Carbon Monoxide and Related Processes

CHAPTER

I

The scientific and industrial importance of the chemistry of carbon monoxide reactions has increased rapidly since about 1900. Studies of the synthesis of methane from water gas (a mixture of about equal parts of hydrogen and carbon monoxide) and the development of the water gas-shift process for hydrogen production were followed by the synthesis of methanol, of higher alcohols, of fatty acids, and of esters. More recent advances include the Fischer-Tropsch process for synthesis of chiefly liquid aliphatic hydrocarbons, alcohols, and minor amounts of aldehydes, fatty acids, and ketones by hydrogenation of carbon monoxide. Research on the Fischer-Tropsch process led to the discovery of the "oxo" process for the addition of carbon monoxide and hydrogen to olefins to produce a particular aldehyde, alcohol, or ketone.

The Fischer-Tropsch synthesis had its origin in an observation made in 1923 by Franz Fischer and Hans Tropsch that alkalized iron turnings at 100–150 atm of hydrogen plus carbon monoxide and 400°–450°C catalyzed the production of "synthol." This product consisted chiefly of oxygenated compounds and a very small quantity of hydrocarbons. At 7 atm and, later, at 1 atm, Fischer found that the distribution of oxygenated and hydrocarbon products was reversed. The first Fischer-Tropsch catalyst was an iron-zinc oxide preparation which was reported by Fischer in 1925. It was tested at atmospheric pressure with a mixture containing 3 volumes of hydrogen and 1 volume of carbon monoxide, and at a temperature of 370°C. However, development of iron catalysts was unsuccessful until 1937, which was several years after the Fischer-Tropsch process was in commercial operation with a cobalt catalyst.

An important advance in the development of Fischer-Tropsch catalysts was the precipitation of nickel-thoria on kieselguhr in 1931. This

catalyst was followed in 1932 by the corresponding cobalt catalyst, 100Co:18ThO_2:100 kieselguhr, parts by weight, which was the starting point in the development of the Ruhrchemie commercial catalyst. Subsequent changes in catalyst composition, concomitant with process development, resulted in a standard composition in 1937 of 100Co: 18ThO_2:200 kieselguhr and in 1938 of 100Co:5ThO_2:8MgO:200 kieselguhr.

The advantages of iron over cobalt, in being easily available from many sources and in imparting flexibility to the process, stimulated continuous research on iron catalysts. In 1937, alkalized precipitated iron catalysts were successfully operated on a laboratory scale by the Kaiser Wilhelm Institut für Kohlenforschung at 15 atm of water gas and at temperatures of 235°–250°C. A German development in 1943–1944 was the preparation of highly active precipitated iron catalysts, which could be operated at 10 atm or atmospheric pressure and a temperature of about 220°C. For the more recently developed Fischer-Tropsch processes, the fluidized and oil-circulation techniques, the development of iron catalysts has shifted toward granules of high mechanical strength. For this purpose, fused catalysts of the synthetic-ammonia type and sintered catalysts prepared from relatively inexpensive, finely powdered iron oxide are being used.

In the Fischer-Tropsch process as developed commercially by the Ruhrchemie A.G. in Germany in 1935–1940, synthesis gas containing 2 volumes of hydrogen per volume of carbon monoxide was compressed to about 7 atm and passed through a granular bed of cobalt catalyst at 185°–205°C. The major products of the synthesis were wax, oil, water, gaseous hydrocarbons, and a minor amount of carbon dioxide. The hydrocarbons were largely straight-chain paraffins. The olefin content varied with pressure, contact time, and temperature. Improved modifications of the Ruhrchemie process involved the recycling of exit gas from the reactor and the use of iron to replace cobalt in catalyst preparation. These changes increased the olefin content of the product and the flexibility of the process, particularly in the control of the proportions of gasoline, Diesel oil, and alcohols.

Application of fluidized-catalyst techniques to the Fischer-Tropsch reaction has yielded a process which produces chiefly motor gasoline with minor amounts (30 per cent) of fuel oil and oxygenated organic compounds. The fluidized-iron-catalyst process is outstanding because of its very high space-time-yield, and because it is competitive with existing petroleum production and refining processes, if natural gas at 5–10 cents per 1,000 cu ft is available as the raw material for synthesis gas production.

In another recently developed process, a cooling oil is circulated through a bed of granular iron catalyst at a rate sufficient to expand the bed and keep the catalyst particles in a state of constant agitation. This process produces a somewhat lower proportion of motor gasoline and correspondingly larger proportions of Diesel oil, fuel oil, and wax than are produced by the fluidized-catalyst process. Although the space-time-yield of the oil-circulation process is only about one-half of that of the fluidized process, much less methane and ethane are made. When coal is used as raw material for synthesis gas production, a low $C_1 + C_2$ yield is essential because of the relatively high cost of the synthesis gas. Further progress in the development of new and improved processes for the Fischer-Tropsch synthesis will be more rapid when the mechanism of the synthesis is more clearly outlined.

Careful determination of the isomeric composition of Fischer-Tropsch gasoline and Diesel oil has yielded some important specifications which any proposed reaction mechanism must meet. Thus, for example, the mechanism of growth of the synthesis molecule must be such as to make the production of a molecule containing a quaternary carbon atom highly improbable. The mechanism must provide for the production of normal alcohols as one of the primary products of the reaction and for the conversion of the alcohols to olefins in the absence of active dehydration catalysts. The proposed mechanism must be also consistent with the results of thermodynamic studies, which show that the isomer distribution is far from equilibrium whereas secondary reactions, such as that between carbon monoxide and water to yield carbon dioxide and hydrogen, are closer to equilibrium on iron catalysts. The reaction mechanism must be in accord also with the extensive chemical changes in the iron catalyst which occur during the synthesis without appreciable effect on activity or product distribution. Although no generally accepted mechanism exists, kinetic studies combined with x-ray diffraction and magnetochemical measurements on catalysts have indicated how more active and more durable catalysts can be prepared.

Scope of the Book

Written primarily for chemists and chemical engineers engaged in Fischer-Tropsch or similar process development, this book presents the basic chemistry of the process, the results of catalyst testing and pilot-plant development work, and data on industrial operations. The first chapter describes the structure and reactivity of hydrogen, carbon monoxide, and the metals commonly used as catalysts, as well as the thermodynamics of reactions of these components. Chapter 2 presents an in-

troduction to heterogeneous catalysis: the methods of studying catalysts and catalytic reactions, and a discussion of three reactions that are somewhat related to those of the Fischer-Tropsch synthesis. Chapter 3 contains a review of the development of catalysts for the hydrocarbon synthesis. Here, catalyst composition and methods of preparation and pretreatment are related to catalytic activity. Chapter 4 presents the laboratory and industrial development of the Ruhrchemie process, as well as more recent pilot-plant developments in Germany and in the United States. The different Fischer-Tropsch processes are classified according to the physical form of the catalyst and the method of removing the heat of the reaction. The productivity, relative efficiency, and versatility of the various processes are compared. This chapter concludes with a brief appraisal of the economic studies of Fischer-Tropsch processes. Chapter 5 describes processes related to the Fischer-Tropsch synthesis, such as the oxo and isoparaffin syntheses. The last chapter relates activity and selectivity of catalysts to the variables of operation and to the phases present in the catalyst during use in the synthesis. The chapter concludes with a critical discussion of the mechanism of the synthesis.

The Structure and Reactivity of Hydrogen, Carbon Monoxide, Iron, Cobalt, and Nickel

The electronic structures of various atoms involved in the Fischer-Tropsch synthesis together with the structures of several of the noble gases are presented in Table 1. The electronic theory of valence is well known, and its details are beyond the scope of this book. It is sufficient to state that in the formation of chemical bonds each constituent atom tends to attain the configuration of the next lower or higher noble gas by donating electrons to or accepting them from other atoms, or by forming electron pair bonds.

About 80 per cent of the bonding energy of the hydrogen molecule is attributed to an electron pair bond, represented as

$$\mathrm{H : H} \qquad (a)$$

the bonding energy being due to the resonance or exchange of electrons between the electronic orbits of the two atoms.[1] To form such a stable

[1] L. Pauling, *Nature of the Chemical Bond*, Cornell University Press, Ithaca, N. Y., 1945.

TABLE 1. ELECTRONIC STRUCTURE OF VARIOUS ELEMENTS INVOLVED IN THE FISCHER-TROPSCH SYNTHESIS

Shell	*K*	*L*		*M*			*N*			*O*	
Orbital	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	5*s*	5*p*
Hydrogen	1										
Helium	2										
Carbon	2	2	2								
Nitrogen	2	2	3								
Oxygen	2	2	4								
Neon	2	2	6								
Argon	2	2	6	2	6						
Potassium	2	2	6	2	6		1				
Iron	2	2	6	2	6	6	2				
Cobalt	2	2	6	2	6	7	2				
Nickel	2	2	6	2	6	8	2				
Copper	2	2	6	2	6	10	1				
Krypton	2	2	6	2	6	10	2	6			
Ruthenium	2	2	6	2	6	10	2	6	7	1	
Xenon	2	2	6	2	6	10	2	6	10	2	6

bond the spins of the two electrons must be opposed. A contribution of about 5 per cent is due to the structures

$$H^+ : H^- \qquad (b)$$

and

$$H^- : H^+ \qquad (c)$$

which would be unstable except for resonance between structures *b* and *c*. The remaining 15 per cent of the bond energy is attributed to complicated interactions not accounted for in a simple treatment of the previous structures. The hydrogen molecule is stable, its bond energy being 102.6 kcal per mole.[1]

Many of the reactions of hydrogen are too well known to merit discussion; hence, only reactions occurring at solid interfaces will be con-

sidered. Hydrogen reduces oxides of heavy metals to the metals or to lower oxides and reduces some carbides and nitrides to metals; oxides, nitrides, and carbides of iron, cobalt, and nickel are reduced to the metal at temperatures above 200°C. Hydrogen is soluble in most metals. With iron, cobalt, nickel, and copper there is no evidence of hydride formation, and the solubility increases with temperature. At 600°C, the solubilities of hydrogen are about 0.5, 1, 1, and 6 cc (STP) per 100 g of copper, cobalt, iron, and nickel, respectively. The solubility of hydrogen in metals that form definite hydrides, such as palladium, zirconium, titanium, thorium, and vanadium, is very much greater, and the solubility decreases with temperature.[2] Hydrogen is chemisorbed on many metals at temperatures as low as −100°C. Most evidence indicates that at least part of the hydrogen is chemisorbed as atoms.

At moderate temperatures, most organic molecules do not react with molecular hydrogen except in the presence of catalysts. Thus, ethylene can be rapidly hydrogenated to ethane on catalysts of many metals at temperatures as low as −100°C, whereas this reaction does not occur to an appreciable extent below 200°C in the absence of catalysts. At temperatures above 150°C in the presence of nickel, cobalt, or iron catalysts, ethylene is hydrogenated to methane. Above 150°C, hydrocracking reactions of other olefinic and paraffinic hydrocarbons can occur on these catalysts. Under suitable conditions of pressure and temperature almost all hydrocarbons or organic molecules containing oxygen or nitrogen can be hydrogenated or hydrocracked in the presence of nickel or other catalysts.

Carbon and oxygen have 4 and 6 valence electrons (L shell), respectively, and the arrangement of these electrons in the carbon monoxide molecule has been the subject of considerable discussion. Pauling[1] postulates the structure to be represented by resonance between

$$:\overset{+}{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{-} \qquad (d)$$

$$:C::\overset{\cdot\cdot}{O}: \qquad (e)$$

$$:\overset{-}{C}:::\overset{+}{O}: \qquad (f)$$

with structures d, e, and f contributing about equally to the normal state of the molecule. The heat of formation of carbon monoxide from atoms of 210 kcal per mole can be compared with 152 kcal per mole for the C=O bond in ketones, which corresponds to a resonance between structures d and e. The difference, 58 kcal per mole, corresponds to the

[2] C. J. Smithells, *Gases and Metals*, John Wiley & Sons, New York, 1937.

energy of resonance with structure *f*. The total resonance energy of carbon monoxide relative to structure *e* is greater than 100 kcal per mole. The zero or very small dipole moment of the molecule is explained by equal contributions of structures *d* and *f*.[3]

The carbon monoxide molecule is very much more stable than radicals such as CH_2 and CCl_2, and there is no tendency for carbon monoxide to polymerize. Most of the reactions of carbon monoxide occur at temperatures above 0°C and then, in many cases, only in the presence of catalysts. The reactions of carbon monoxide and hydrogen are summarized in Table 2. Reaction *F* probably occurs to a limited extent in the Fischer-Tropsch synthesis.

Table 2. Reactions of Carbon Monoxide and Hydrogen

	Catalysts	Promoters	Temperature, °C	Pressure, atm	Product
A. Methane synthesis	Ni	ThO_2, MgO	250–500	1	Chiefly methane
B. Fischer-Tropsch synthesis	Fe, Co, Ni	ThO_2, MgO, Al_2O_3, K_2O	150–350	1–30	Paraffinic and olefinic hydrocarbons varying from methane to waxes, plus small to large quantities of oxygenated products
	Ru		150–250	100–1,000	High-molecular-weight paraffinic hydrocarbons
C. Methanol synthesis	ZnO, Cu, Cr_2O_3, MnO		200–400	100–1,000	Methanol
D. Higher alcohol synthesis	Same as in *C*	Alkali	300–450	100–400	Methanol and higher alcohols
E. Iso synthesis	ThO_2, ZnO + Al_2O_3	K_2O	400–500	100–1,000	Saturated branched hydrocarbons
F. Oxo synthesis [a]	Co, Fe		100–200	100–200	Oxygenated organic compounds

[a] This reaction involves hydrogen, carbon monoxide, and olefins.

Carbon monoxide reacts with aqueous solutions of sodium hydroxide to form sodium formate at 100°–200°C and 5–8 atm. At higher pressures, carbon monoxide reacts with aqueous solutions of salts and mineral acids to form formic acid. Carbon monoxide and water vapor are readily converted to carbon dioxide and hydrogen—the water-gas reaction—at

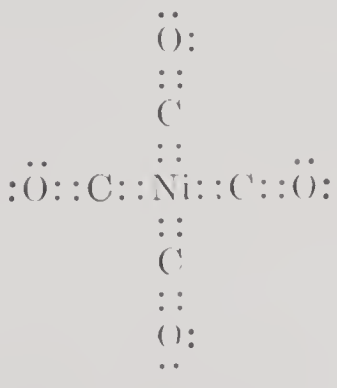
[3] The resonance structures *d*, *e*, and *f* of Pauling are not universally accepted. L. H. Long and A. D. Walsh, *Trans. Faraday Soc.*, **43**, 342 (1947), presented evidence for structure *e*. Fajans, *Chem. Eng. News*, **27**, 900 (1949), suggested a structure represented by (C^{4+}) $10e^-$ (O^{6+}) in which the ten valence electrons are quantized with respect to the C^{4+} and O^{6+} cores and move predominantly in the binding region between the cores. The electron density near the C^{4+} and O^{6+} must be proportional to the core charges to explain the low dipole moment.

200°–300°C and atmospheric pressure in the presence of iron chromite, cobalt chromite, and other catalysts. Reppe [4] has developed new reactions and processes involving reactions of acetylenes or olefins with carbon monoxide, metal carbonyls, or hydrocarbonyls as illustrated by the equations for the preparation of acrylic acid and *n*-propyl alcohol:

$$4C_2H_2 + Ni(CO)_4 + 4H_2O + 2HCl \rightarrow 4H_2C{=}CHCOOH + NiCl_2 + H_2 \quad (1)$$

$$2C_2H_4 + H_2Fe(CO)_4 + 4H_2O \rightarrow 2CH_3CH_2CH_2OH + Fe(HCO_3)_2 \quad (2)$$

In the presence of metals, carbon monoxide reacts in a number of ways. At low temperatures many metals such as cobalt, nickel, iron, and copper tenaciously chemisorb carbon monoxide. From room temperature to about 200°C carbonyls such as $Fe(CO)_5$, $Ni(CO)_4$, and $[Co(CO)_4]_2$ are formed. These carbonyls are liquids which boil below 50°C and decompose at atmospheric pressure at temperatures below 150°C. In the volatile carbonyls, as well as in iron and cobalt hydrocarbonyls, the 3*d* and 4*p* orbitals of the metal are filled with electrons donated by carbon monoxide and hydrogen so that the metal atom attains the electronic structure of krypton with 36 electrons. In the formula postulated for nickel carbonyl (*g*), the nickel atom is surrounded



(*g*)

by its 28 extranuclear electrons plus 2 each from the carbon monoxide.[1] This rare-gas-type structure accounts for the low melting and boiling points of this high-molecular-weight substance. In a similar structure for cobalt carbonyl, $Co(CO)_4$, the number of electrons about the cobalt atom is 35; this carbonyl occurs as a dimer in which each cobalt atom is surrounded by 36 electrons. Cobalt hydrocarbonyl, $HCo(CO)_4$, in which hydrogen contributes an electron to complete the krypton struc-

[4] J. W. Reppe, *Acetylene Chemistry*, O.T.S.-PB Report 18852-s, Charles A. Meyer and Co., New York, 1949.

ture, acts as a strong acid in solution. In iron carbonyl, $Fe(CO)_5$, and hydrocarbonyl, $H_2Fe(CO)_4$, the number of electrons surrounding the metal atom is again 36. The iron hydrocarbonyl acts as a weak monobasic acid in solution. Hydrocarbonyls of nickel have not been prepared. Non-volatile crystalline carbonyls such as $Fe_2(CO)_9$ and $Fe(CO)_4$ have been prepared.

At temperatures of 150°–250°C, carbon monoxide reacts with iron, cobalt, and nickel to form carbides such as Fe_2C, Co_2C, and Ni_3C. At temperatures above 250°–350°C, these carbides decompose to metal and carbon or lower carbides. Above 300°C, carbon monoxide decomposes on these metals to produce chiefly free carbon and carbon dioxide. At least at the lower temperatures, there is evidence to indicate that carbon deposition may occur by formation and decomposition of carbides.[5]

In many reactions, such as hydrogenation, the high activity of catalysts of iron, cobalt, and nickel, as compared with catalysts of copper or silver, has been attributed to the presence of unfilled 3*d* orbitals in iron, cobalt, and nickel.[6] However, present theories relating electronic structure of catalysts to activity have not been completely developed or tested.

Thermodynamics of the Fischer-Tropsch Synthesis and Related Reactions

In the remainder of this chapter the thermodynamics of the Fischer-Tropsch synthesis and related reactions will be discussed. It should be emphasized that these data indicate only the possible extent to which the reactions can proceed as defined by their equilibrium constants. How nearly the reaction approaches equilibrium depends upon the rate of reaction and elapsed time, and in flowing systems upon the rate and space velocity. If two or more reactions are thermodynamically possible from the same reactants, the products formed depend upon rates of the possible reactions and rates of transformation of the products to more stable forms. The purpose of a catalyst is to accelerate the rate at which one or more of the thermodynamically possible reactions approach equilibrium. The ideal catalyst in a system in which several reactions are possible is one which accelerates only the reactions producing the desired products.

The thermodynamic data of the hydrogenation of carbon monoxide and dioxide to hydrocarbons, as well as various reactions of hydrocarbons, have been computed from the thermodynamic tables of the

[5] L. J. E. Hofer, *U. S. Bur. Mines Repts. Invest.* 3,770 (1944).
[6] D. A. Dowden and P. W. Reynolds, *Nature*, **164**, 50 (1949).

American Petroleum Institute,[7] which are the best available thermal data. The thermodynamics of the Fischer-Tropsch synthesis have been discussed by Smith [8] and Myddleton.[9] Only a relatively few compounds were considered by these authors, and some of the results of Smith appear to have been based upon unreliable thermodynamic data, *eg*, the equilibrium constants for the synthesis of methanol. The thermodynamics of the incorporation of methane in the Fischer-Tropsch reaction has been discussed by Prettre.[10] Thermodynamic results presented in this chapter for the synthesis of alcohols, the reduction of oxides and carbides, and the formation of carbonyls represent what appear to be the best available data. In the data presented in this chapter, the standard state of all gaseous components is 1 atm.

HYDROGENATION OF CARBON MONOXIDE AND CARBON DIOXIDE

Hydrocarbons from Carbon Monoxide and Hydrogen

Reactions producing paraffinic and olefinic hydrocarbons may be represented by equations $3A$, $3B$, $4A$, and $4B$, where 3 and 4 represent reactions yielding paraffins and olefins, respectively, and A and B denote reactions yielding water and carbon dioxide, respectively.

$$(2n + 1)H_2 + nCO = C_nH_{2n+2} + nH_2O \qquad (3A)$$

$$2nH_2 + nCO = C_nH_{2n} + nH_2O \qquad (4A)$$

$$(n + 1)H_2 + 2nCO = C_nH_{2n+2} + nCO_2 \qquad (3B)$$

$$nH_2 + 2nCO = C_nH_{2n} + nCO_2 \qquad (4B)$$

Similar equations can be written for the production of other hydrocarbons such as cyclic compounds and diolefins.

The heats of these reactions are of great practical interest, since the removal of this heat from the reactor is one of the most difficult engineering problems of the synthesis. Heat-of-reaction data for many of the common hydrocarbons at 127°, 227°, and 427°C are given in Table 3. The columns marked A contain data for reactions yielding water ($3A$ and $4A$) and columns marked B, carbon dioxide ($3B$ and $4B$). The heat evolved in reactions of type B is about 9 kcal per mole more negative

[7] F. D. Rossini and coworkers, American Petroleum Institute, *Research Project* 44, National Bureau of Standards.

[8] D. L. Smith, *Ind. Eng. Chem.*, **19**, 801 (1927).

[9] W. W. Myddleton, *J. Inst. Petroleum*, **30**, 211 (1944).

[10] M. Prettre, *Rev. inst. franç. pétrole et Ann. combustibles liquides*, **2**, 131 (1947).

per carbon atom of the hydrocarbon product than that of the corresponding type *A* reaction. The high negative heats of reaction imply that the equilibrium constants decrease rapidly with increasing temperature.

TABLE 3. HEATS OF REACTIONS YIELDING HYDROCARBONS BY HYDROGENATION OF CARBON MONOXIDE

Hydrocarbon	ΔH, kcal per mole [a]					
	Reaction *A* [b]			Reaction *B* [c]		
	127°C	227°C	427°C	127°C	227°C	427°C
Graphite, C	− 31.725	− 31.981	− 32.302	− 41.435[d]	− 41.501[d]	− 41.353[d]
Methane, CH_4	− 50.354	− 51.283	− 52.703	− 60.064	− 60.803	− 61.754
Ethane, C_2H_6	− 84.869	− 86.399	− 88.584	−104.289	−105.439	−106.686
Ethylene, C_2H_4	− 51.684	− 52.824	− 54.462	− 71.104	− 71.864	− 72.564
Acetylene, C_2H_2	− 9.316	− 9.913	− 10.817	− 28.736	− 28.953	− 28.919
Propane, C_3H_8	−121.533	−123.565	−126.396	−150.663	−152.125	−153.549
Propylene, C_3H_6	− 91.417	− 93.150	− 95.606	−120.547	−121.710	−122.759
Methyl acetylene, C_3H_4	− 51.400	− 52.663	− 54.483	− 80.530	− 81.223	− 81.636
n-Butane, C_4H_{10}	−158.529	−161.052	−164.488	−197.369	−199.132	−200.692
1-Butene, C_4H_8	−127.990	−130.139	−133.088	−166.830	−168.219	−169.292
n-Hexane, C_6H_{14}	−232.730	−236.246	−240.962	−290.990	−293.366	−295.268
1-Hexene, C_6H_{12}	−202.250	−205.386	−209.612	−260.510	−262.506	−263.918
Cyclohexane, C_6H_{12}	−220.050	−225.965	−230.402	−280.310	−283.085	−284.708
Benzene, C_6H_6	−171.796	−174.350	−177.772	−230.056	−231.584	−232.078
Methyl cyclohexane, C_7H_{14}	−261.865	−265.787	−270.614	−329.835	−332.427	−333.971
Toluene, C_7H_8	−211.748	−214.862	−219.047	−279.718	−281.502	−282.404
n-Octane, C_8H_{18}	−306.630	−311.148	−317.126	−384.310	−387.308	−389.534
1-Octene, C_8H_{16}	−276.200	−280.248	−285.816	−353.880	−356.408	−358.224
n-Decane, $C_{10}H_{22}$	−380.530	−386.040	−393.290	−477.630	−481.240	−483.800
1-Decene, $C_{10}H_{20}$	−350.050	−355.521	−361.920	−447.150	−450.410	−452.430
n-Eicosane, $C_{20}H_{42}$	−750.000	−760.500	−774.080	−944.200	−950.900	−955.100
1-Eicosene, $C_{20}H_{40}$	−719.500	−729.620	−742.740	−913.700	−920.020	−923.760

[a] Computed from data of reference 7.
[b] Reaction *A* involves the formation of hydrocarbon plus water.
[c] Reaction *B* involves the formation of hydrocarbon plus carbon dioxide.
[d] This reaction ($2CO = C_g + CO_2$) does not involve hydrogen.

These data are also illustrated by Figure 1, in which the heat of reaction per carbon atom of the hydrocarbon produced by reactions of

type *A* is plotted against temperature. The heats of reaction are not very dependent upon temperature. The heats of reactions yielding saturated hydrocarbons per carbon atom decrease with carbon number, while similar heats of reaction for olefins increase with carbon number;

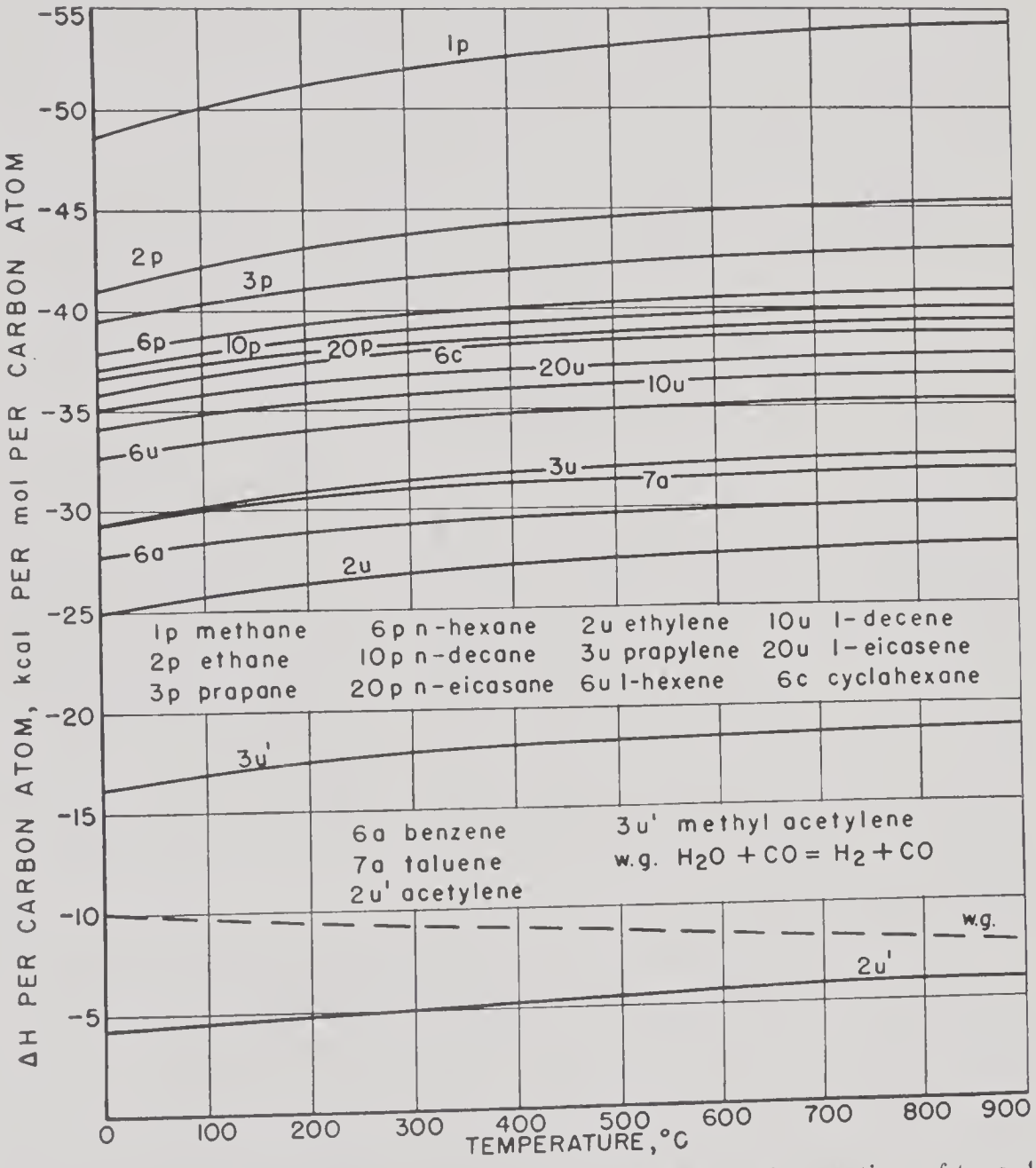


FIGURE 1–1. Heats of reaction of formation of hydrocarbons by reactions of type *A* (water as the oxygenated product), expressed as kilocalories per mole per carbon atom of the hydrocarbon. Heats of reactions of type *B* (carbon dioxide as the oxygenated product) are obtained by adding the heat of reaction of the water-gas reaction (w.g.) to the heats for reaction of type *A*.

both series approach limits near the lines of C_{20} paraffins and olefins. Heats of reactions of type *B* may be obtained by adding the heat of the water-gas reaction (wg) to those of reaction *A*. In Table 3 and Figure 1,

heats of formation of branched-chain saturated and unsaturated hydrocarbons were not included, because their heats of reaction are nearly equal to those of the corresponding straight-chain isomer.

To illustrate the magnitude of the heat of reaction the following examples were computed from data of Table 3. The heat evolved in the formation of *n*-decane and 1-decene by reaction *A* and *B* at 200°C, expressed in kilocalories per gram and British thermal units per pound of hydrocarbons, is shown below:

Reaction	*A* kcal per g	*A* Btu per lb	*B* kcal per g	*B* Btu per lb
n-decane	2.71	4,880	3.38	6,090
1-decene	2.53	4,560	3.21	5,780

The heat evolved in the consumption of a cubic meter (STP) of $2H_2 + 1CO$ gas to form 1-decene by reaction *A* is 527 kcal, and that of a cubic meter (STP) of $1H_2 + 2CO$ gas reacting to form 1-decene by reaction *B* is 669 kcal.

The method of using Figure 1 is illustrated by the estimation of the heat of the reactions producing 1-nonene by reactions yielding water (*A*) and carbon dioxide (*B*), at 300°C. By interpolating between the lines for 1-hexene (6u) and 1-decene (10u), the value of ΔH per carbon atom by reaction *A* may be estimated as −36 kcal, and the heat of reaction (−36) (9) = −324 kcal per mole. For reaction *B*, the value of the water-gas reaction, −9.0 kcal, is added to the value of ΔH per carbon atom, and this sum multiplied by 9 gives −405 kcal per mole.

In Tables 4 and 5 are given the logarithms of the equilibrium constants of the formation of hydrocarbons by the Fischer-Tropsch synthesis according to reactions *A* and *B*. The equilibrium constants for the formation of paraffinic hydrocarbons by reactions 3*A* and 3*B* are defined as follows:

$$K_{eq} = \frac{p_{C_nH_{2n+2}} p^n{}_{H_2O}}{p^{2n+1}_{H_2} p^n_{CO}} \quad \text{and} \quad K_{eq} = \frac{p_{C_nH_{2n+2}} p^n{}_{CO_2}}{p^{n+1}_{H_2} p^{2n}_{CO}}$$

respectively, with the partial pressures in atmospheres. Equilibrium constants for the formation of other hydrocarbons are defined in a similar manner. For exact calculations, fugacities rather than partial pressures should be used; however, at low-to-moderate pressures (1–30 atm), such as are usually employed in the Fischer-Tropsch synthesis, the errors introduced by using partial pressures are quite small. The equilibrium constants for formation of branched-chain saturated and unsaturated hydrocarbons by reactions of types *A* and *B* usually do not differ from those of the straight-chain isomer by more than a factor of ten; hence,

no data are given for these reactions. It should be noted that, in general, a straight-chain hydrocarbon is somewhat less stable thermodynamically than its branched isomers (see Table 9).

TABLE 4. EQUILIBRIUM CONSTANTS FOR REACTIONS PRODUCING HYDROCARBONS FROM HYDROGEN AND CARBON MONOXIDE, WITH WATER AS OXYGENATED PRODUCT [a]

Compound	$\log_{10} K_{eq}$							Temperature at Which $K_{eq} = 1$, °C
	27°C	127°C	227°C	327°C	427°C	627°C	827°C	
Graphite, C	15.858	10.113	6.633	4.296	2.618	+ 0.372	− 1.061	671
Methane, CH_4	24.677	15.603	10.060	6.296	3.571	− 0.116	− 2.496	620
Ethane, C_2H_6	37.388	22.109	12.755	6.417	1.835	− 4.356	− 8.338	476
Ethylene, C_2H_4	19.839	10.569	4.853	0.973	− 1.843	− 5.655	− 8.115	358
Acetylene, C_2H_2	− 4.689	− 6.315	− 7.364	− 8.103	− 8.656	− 9.426	− 9.939	<0
Propane, C_3H_8	51.612	29.688	16.301	7.241	0.697	− 8.123	− 13.781	440
Propylene, C_3H_6	36.610	20.171	10.085	3.250	− 1.697	− 8.378	− 12.677	389
Methyl acetylene, C_3H_4	13.714	+ 4.503	− 1.180	− 5.053	− 7.868	−11.684	− 14.150	205
Butane, C_4H_{10}	66.052	37.482	20.032	8.228	− 0.297	−11.766	− 19.121	423
1-Butene, C_4H_8	50.816	27.773	13.667	4.126	− 2.767	−12.055	− 18.017	383
Butadiene, C_4H_6	36.854	18.665	7.528	− 0.010	− 5.457	−12.795	− 17.506	325
n-Hexane, C_6H_{14}	94.931	52.969	27.356	10.049	− 2.439	−19.233	− 29.992	405
1-Hexene, C_6H_{12}	79.857	43.404	21.131	6.080	− 4.782	−19.397	− 28.765	379
Cyclohexane, C_6H_{12}	89.457	49.392	24.903	8.345	− 3.600	−19.652	− 29.897	393
Benzene, C_6H_6	72.525	41.551	22.644	9.873	+ 0.658	−11.738	− 19.684	435
Methyl cyclohexane, C_7H_{14}	106.060	58.857	30.033	10.566	− 3.466	−22.306	− 34.338	399
Toluene, C_7H_8	89.639	51.455	28.154	12.415	+ 1.061	−14.212	− 24.000	438
n-Octane, C_8H_{18}	123.611	68.305	34.564	11.775	− 4.665	−26.757	− 40.905	395
1-Octene, C_8H_{16}	108.531	58.738	28.340	7.808	− 7.006	−26.922	− 39.677	376
n-Decane, $C_{10}H_{22}$	152.283	83.637	41.770	13.499	− 6.890	−34.283	− 51.817	390
1-Decene, $C_{10}H_{20}$	137.203	74.068	35.547	9.530	− 9.231	−34.449	− 50.589	373
n-Eicosane, $C_{20}H_{42}$	295.641	160.295	77.802	22.190	−18.019	−71.913	−106.376	378
1-Eicosene, $C_{20}H_{40}$	280.561	150.726	71.578	18.150	−20.361	−72.078	−105.149	370

[a] Computed from data of reference 7.

To illustrate the thermodynamics of the reactions producing various hydrocarbons, the standard-state free-energy changes per carbon atom of the hydrocarbon by reactions of type *A* are plotted against temperature in Figures 2, 3, and 4. These curves represent the tendency for the various reactions to occur. Negative free-energy changes correspond to reactions with equilibrium constants greater than one, as given by the

TABLE 5. EQUILIBRIUM CONSTANTS FOR REACTIONS PRODUCING HYDROCARBONS FROM HYDROGEN AND CARBON MONOXIDE, WITH CARBON DIOXIDE AS OXYGENATED PRODUCT [a]

Compound	$\log_{10} K_{eq}$							Temperature at Which $K_{eq} = 1$, °C
	27°C	127°C	227°C	327°C	427°C	627°C	827°C	
Graphite, C [b]	20.811	13.283	8.753	5.729	3.573	+ 0.716	− 1.086	697
Methane, CH_4	29.630	18.773	12.180	7.729	4.526	1.203	− 2.521	643
Ethane, C_2H_6	47.294	28.449	16.995	9.283	3.745	− 3.670	− 8.388	516
Ethylene, C_2H_4	29.745	16.909	9.093	3.839	+0.067	− 4.967	− 8.165	429
Acetylene, C_2H_2	5.217	+ 0.025	− 3.124	− 5.238	−6.746	− 8.740	− 9.989	128
Propane, C_3H_8	66.471	39.198	22.661	11.540	3.562	− 7.094	− 13.856	483
Propylene, C_3H_6	51.469	29.681	16.445	7.549	1.168	− 7.347	− 12.752	449
Methyl acetylene, C_3H_4	28.573	14.013	5.180	+ 0.754	−5.003	−10.655	− 14.225	338
n-Butane, C_4H_{10}	85.864	50.162	28.512	13.958	+3.523	−10.394	− 19.221	468
1-Butene, C_4H_8	70.628	40.453	22.147	9.858	+1.053	−10.683	− 18.116	441
1,3-Butadiene, C_4H_6	56.664	31.345	16.008	5.721	−1.637	−11.423	− 17.606	405
n-Hexane, C_6H_{14}	124.649	71.990	40.076	18.644	3.291	−17.172	− 30.142	453
1-Hexene, C_6H_{12}	109.572	62.425	33.851	14.676	0.948	−17.336	− 28.915	435
Cyclohexane, C_6H_{12}	119.173	68.412	37.623	16.940	2.130	−17.592	− 30.047	444
Benzene, C_6H_6	102.243	60.571	35.364	18.468	6.388	− 9.678	− 19.834	494
Methyl cyclohexane, C_7H_{14}	140.728	81.047	44.873	20.594	3.221	−19.902	− 34.513	449
Toluene, C_7H_8	124.307	73.645	42.994	22.444	7.746	−11.808	− 24.175	494
n-Octane, C_8H_{18}	163.232	93.665	51.524	23.236	2.977	−24.013	− 41.105	444
1-Octene, C_8H_{16}	144.325	84.099	45.300	19.269	+0.636	−24.178	− 39.877	431
n-Decane, $C_{10}H_{22}$	201.809	115.337	62.970	27.825	2.660	−30.849	− 52.067	439
1-Decene, $C_{10}H_{20}$	186.729	105.768	56.747	23.856	0.319	−31.015	− 50.839	428
n-Eicosane, $C_{20}H_{42}$	394.693	223.695	120.200	50.771	1.081	−65.045	−106.876	429
1-Eicosene, $C_{20}H_{40}$	379.612	214.126	113.976	46.802	−1.257	−65.210	−105.649	425

[a] Computed from data of reference 7.

[b] This reaction ($2CO = C_g + CO_2$) does not involve hydrogen.

usual definition, $-\Delta F^\circ = RT \ln K_{eq}$, where ΔF° is the standard-state free-energy change. Included in Figures 2, 3, and 4 is the free-energy change for the water-gas reaction. Free-energy changes for formation of hydrocarbons by reactions of type *B* are obtained by adding the water-gas reaction curve (wg) to that for the formation of that hydrocarbon by reaction *A*.

The curves in Figures 2–4 approximate straight lines, a consequence of the nearly constant standard-state enthalpy and entropy changes.

The lines for paraffinic hydrocarbons (Figure 2) are nearly parallel and approach a limit near the line for *n*-eicosane as the molecular weight increases. The lines for mono-olefins (Figure 3) have different slopes, and as the molecular weight is increased the lines shift in both slope and

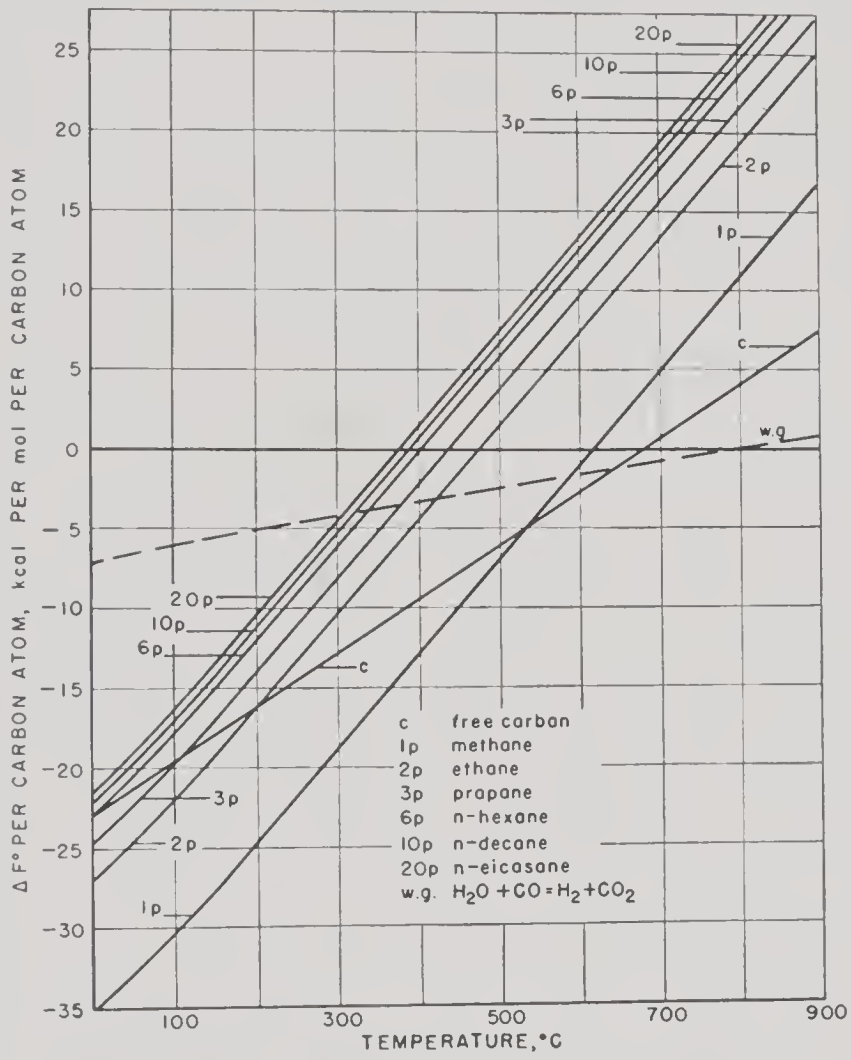


FIGURE 1–2. Standard-state free energies of formation of paraffins by reactions of type *A* (water as the oxygenated product), expressed as kilocalories per mole per carbon atom of the hydrocarbon. Standard-state free energies of reactions of type *B* (carbon dioxide as the oxygenated product) may be obtained by adding the free energy of the water-gas reaction (w.g.) to the free energies of reactions to type *A*.

position, the line for 1-eicosene being only slightly different from that for *n*-eicosane. The free energies of reactions forming acetylenic, diolefinic, aromatic, and alicyclic hydrocarbons are compared with those of methane and *n*-eicosane in Figure 4.

As an example of the method of using Figures 2, 3, and 4, the free-energy changes and equilibria of reactions yielding 1-nonene according to reactions forming water (*A*) and carbon dioxide (*B*) at 300°C are estimated as follows. From Figure 3 by interpolating between the lines

6u and 10u, ΔF° per carbon atom for reaction A is estimated as -4.0 kcal; this value multiplied by the number of carbon atoms (9) gives -36.0 kcal per mole. For the reaction of type B, the value of ΔF° for the water-gas reaction at 300°C (-3.9 kcal) is added to -4.0 kcal, to give $\Delta F^\circ = -7.9$ kcal per carbon atom or -71.1 kcal per mole. The

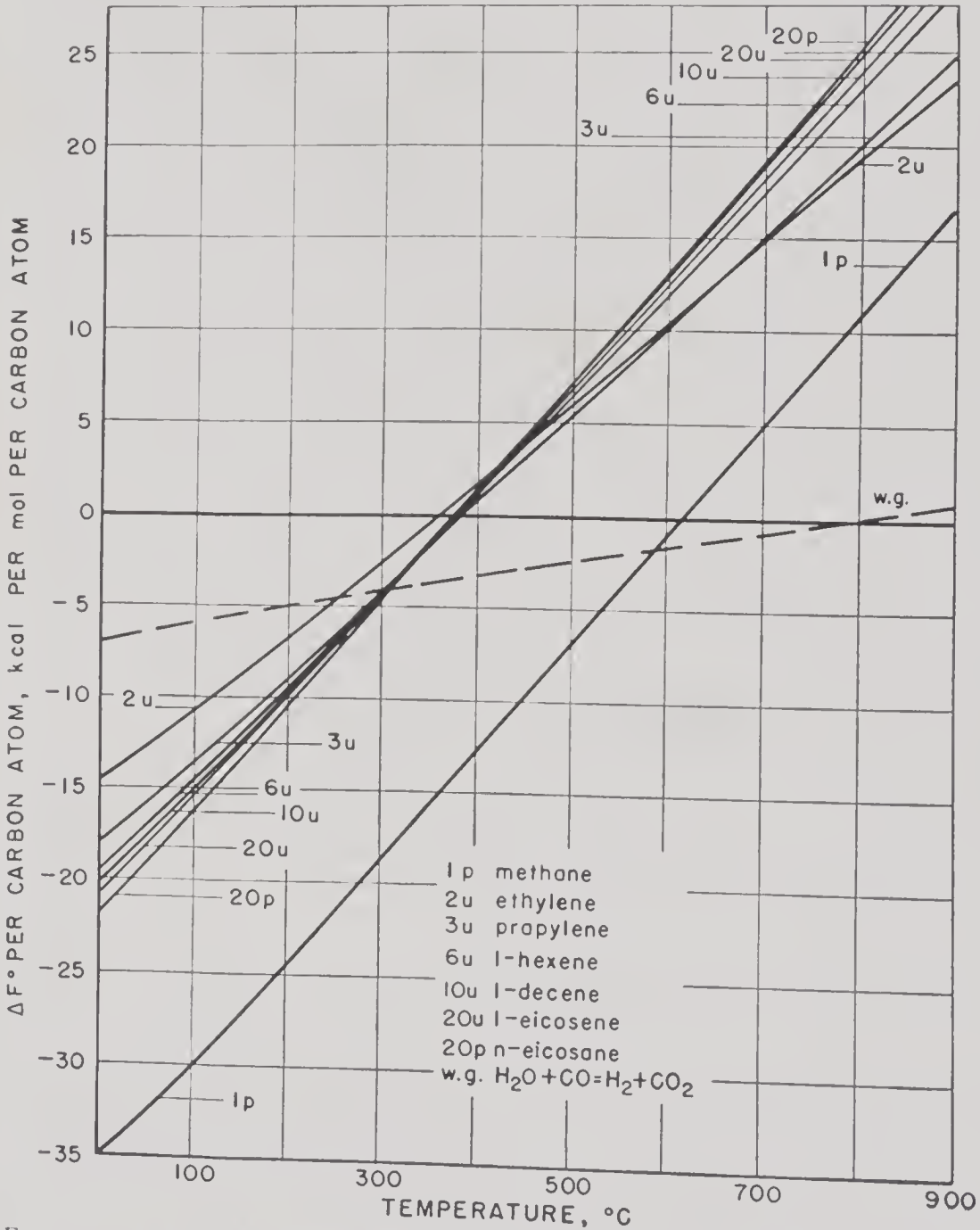


FIGURE 1–3. Standard-state free energies of formation of olefins by reactions of type A (water as the oxygenated product), expressed as kilocalories per mole per carbon atom of the hydrocarbon. Standard-state free energies of reactions of type B (carbon dioxide as the oxygenated product) may be obtained by adding the free energy of the water-gas reaction (w.g.) to the free energies of reactions of type A.

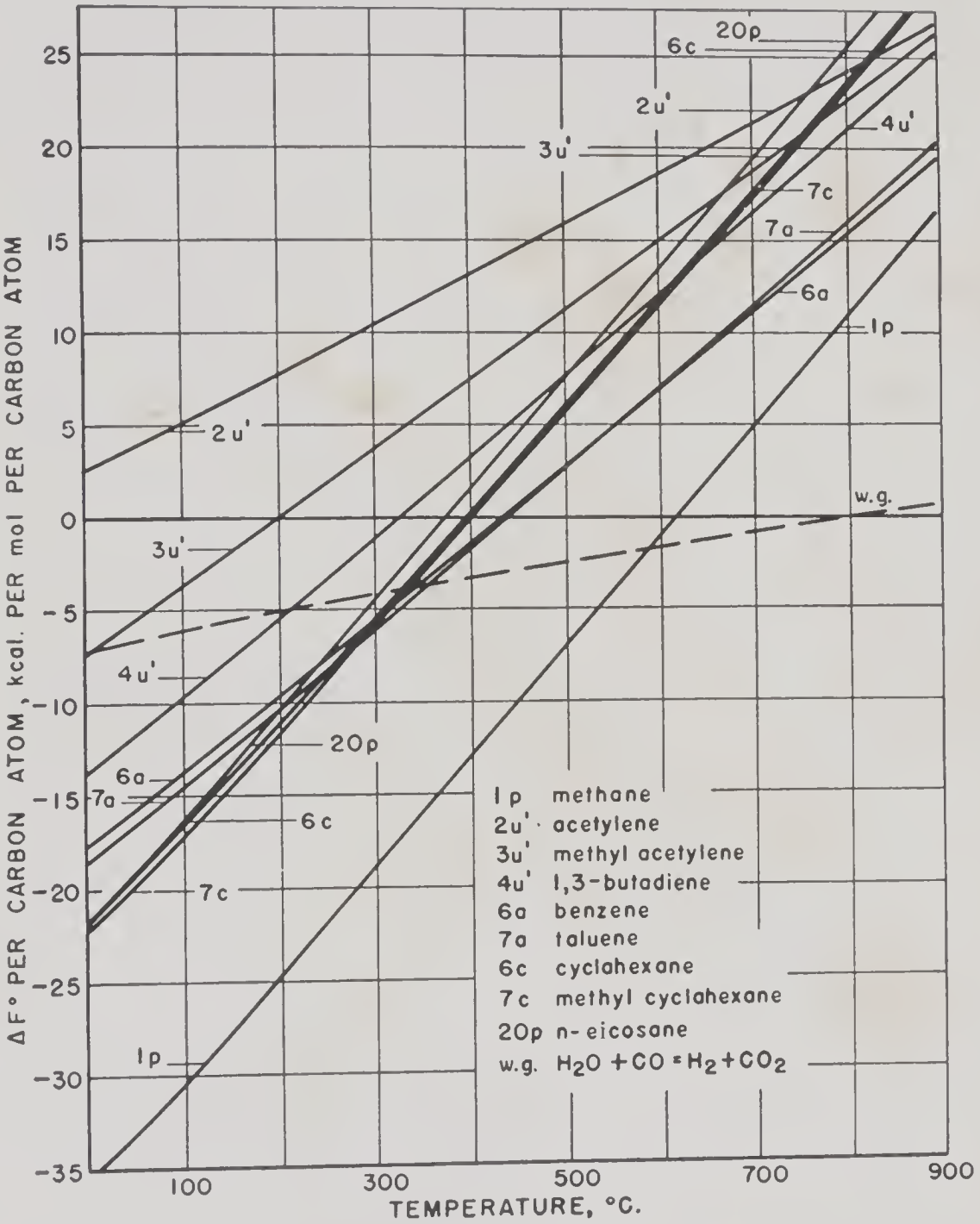


FIGURE 1–4. Standard-state free energies of formation of various types of hydrocarbons by reactions of type *A* (water as the oxygenated product), expressed as kilocalories per mole per carbon atom of the hydrocarbon. Standard-state free energies of reactions of type *B* (carbon dioxide as the oxygenated product) may be obtained by adding the free energy of the water-gas reaction (w.g.) to the free energies of reactions of type *A*.

equilibrium constant may then be computed from the standard free-energy change as follows, for reaction B:

$$-\Delta F^\circ = 71.1 = RT \ln K_{eq} = 4.6 \times 573 \log_{10} K_{eq}$$

and

$$K_{eq} = 10^{27}$$

From the equilibrium constants the highest attainable conversion of hydrogen and carbon monoxide may be computed. At a constant temperature, the conversions at equilibrium for the reactions in Tables 4 and 5 increase with operating pressure; therefore, it is difficult to suggest any range of values of the equilibrium constant below which the equilibrium conversion is too low to be practical. As a rough approximation, the temperature at which equilibrium constants equal one ($\Delta F^\circ = 0$) has been taken as the maximum temperature for which appreciable conversions may be obtained. These temperatures are given in Tables 4 and 5 and may be estimated from Figures 2, 3, and 4.

For the formation of paraffin hydrocarbons by reaction A, the temperature at which $K_{eq} = 1$ decreases from 620°C for methane to 378°C for *n*-eicosane, and for reaction B the corresponding temperatures are 643° and 429°C. For olefins by reaction A these temperatures increase from 358°C for ethylene to 389°C for propylene and then decrease to 370°C for 1-eicosane. Corresponding temperatures of olefin formation by reaction B are 429°, 449°, and 425°C, respectively. The temperatures at which $K_{eq} = 1$ for formation of 1,3-butadiene, methyl acetylene, and acetylene by reaction A are 325°, 205°, and <0°C and by reaction B, 405°, 338°, and 128°C, respectively. For cyclohexane and methyl cyclohexane, $K_{eq} = 1$ at about the same temperatures as *n*-hexane and *n*-heptane. For benzene and toluene these temperatures are 435° and 438°C for reaction A and 494° and 494°C for reaction B.

The data in Tables 4 and 5 and in Figures 2, 3, and 4 may be summarized as follows:

1. Reactions that form carbon dioxide (type B) have larger equilibrium constants (more negative values of ΔF°) than corresponding reactions yielding water (type A) at the same temperatures. Thus, reactions of type B are thermodynamically possible at higher temperatures than corresponding reactions of type A.

2. The free-energy changes per carbon atom of the hydrocarbon of reactions forming methane are more negative than those for corresponding reactions yielding higher hydrocarbons. Below 500°C, the reactions producing carbon (graphite) are less negative than those yielding methane but more negative than reactions yielding higher hydrocarbons.

3. The practical upper temperature limit of the formation of higher hydrocarbons of any type is about 500°C.

4. For molecules containing the same number of carbon atoms the free energy of the synthesis reactions become more negative in the following order—diolefins, mono-olefins, and paraffins. The formation of sizable amounts of acetylene is thermodynamically impossible at usual synthesis temperatures and pressures.

5. The formation of branched-chain, cyclic, and aromatic hydrocarbons is thermodynamically possible.

6. The hydrocarbons formed in the Fischer-Tropsch synthesis, chiefly normal hydrocarbons and α-olefins, indicate that the process does not proceed to the state of lowest free energy. The course of the reaction is determined by the catalytic mechanism.

Hydrogenation of Carbon Dioxide

The data in Table 6 for hydrogenation of carbon dioxide indicate that at moderate pressures it is possible to produce paraffinic hydrocarbons at temperatures below 350°C and olefins below about 250°C. The free-energy changes of these reactions are considerably less negative than those of hydrogenation of carbon monoxide. Heats of these reactions and their standard free-energy changes may be estimated from Figures 1–4 by subtracting the contribution of the water-gas reaction from the values estimated from the heat of reaction or free-energy curves and multiplying by the number of carbon atoms in the hydrocarbon. The temperatures at which $\Delta F^\circ = 0$ ($K_{eq} = 1$) are given by the intersection of

Table 6. Equilibrium Constants for Hydrogenation of Carbon Dioxide [a]

	$\log_{10} K_{eq}$			
Hydrocarbon	127°C	227°C	327°C	427°C
Methane, CH_4	12.433	7.940	4.864	2.616
Ethane, C_2H_6	15.769	8.515	3.552	− 0.076
Ethylene, C_2H_4	4.229	0.614	−1.892	− 3.753
Propane, C_3H_8	20.178	9.941	2.944	− 2.169
Propene, C_3H_6	10.661	3.726	−1.047	− 4.563
n-Butane, C_4H_{10}	24.802	11.553	2.497	− 4.117
1-Butene, C_4H_8	15.093	5.187	−1.604	− 6.588
n-Decane, $C_{10}H_{22}$	51.937	20.571	−0.827	−16.440
1-Decene, $C_{10}H_{20}$	42.367	14.348	−4.796	−18.783

[a] Reference 7.

the free-energy curves for the hydrocarbons and that for the water-gas reaction. Despite the fact that hydrogenation of carbon dioxide is possible under most conditions of the synthesis, sizable amounts of carbon dioxide are produced during the hydrogenation of carbon monoxide, especially with iron catalysts.

Hydrogenation of Carbon Monoxide to Alcohols

Table 7 presents equilibrium constants for the hydrogenation of carbon monoxide to alcohols according to the reaction,

$$2nH_2 + nCO = C_nH_{2n+1}OH + (n - 1)H_2O \qquad (5)$$

The data indicate that it is not possible to produce sizable amounts of methanol at temperatures and pressures normally used for the Fischer-Tropsch synthesis (1–30 atm and 150°–350°C). The values of the equilibrium constants increase with the number of carbon atoms in the alcohol, and the temperatures at which the equilibrium constants equal one increase from about 260°C for ethanol to >327°C for butanol-1 and hexanol-1. Hence, sizable amounts of ethanol and higher alcohols may be obtained under usual conditions of the synthesis.

Table 7. Synthesis of Alcohols

$$2nH_2 + nCO = C_nH_{2n+1}OH + (n - 1)H_2O$$

Alcohol	$\log_{10} K_{eq}$							
	127°C	225°C	227°C	250°C	300°C	325°C	327°C	400°C
Methanol		−2.215 [a]		−2.635 [a] −2.801 [b]	−3.824 [b]	−4.328 [c]		−4.921 [d]
Ethanol	+ 9.735 [e]		2.826 [e]		−1,770 [f]		−1.849 [e]	−6,081 [f]
	9.909 [g]		2.960 [g]				−1.747 [g]	
Propanol-1	17.968 [g]		6.814 [g]				−0.741 [g]	
Butanol-1	26.012 [g]		10.703 [g]				+0.344 [g]	
Hexanol-1	41.098 [g]		17.474 [g]				1.485 [g]	

[a] R. H. Newton and B. F. Dodge, *J. Am. Chem. Soc.*, **56**, 1,287 (1934).
[b] B. S. Lacy, R. G. Dunning, and H. H. Storch, *ibid.*, **52**, 926 (1930).
[c] D. M. Newitt, B. J. Byrne, and H. W. Strong, *Proc. Roy. Soc. (London) (A)*, **123**A, 236 (1929).
[d] E. Audibert and A. Raineau, *Ind. Eng. Chem.*, **20**, 1,105 (1928).
[e] F. G. Briekwedde, M. Moskow, and J. G. Aston, *J. Research Natl. Bur. Standards*, **37**, 263 (1946).
[f] D. L. Smith, *Ind. Eng. Chem.*, **19**, 801 (1927).
[g] These equilibrium constants are calculated from approximate thermodynamic data for the dehydration of alcohols reported by R. R. Wenner, *Chem. Eng. Progress*, **45**, 194 (1949).

Alcohols are produced in the Fischer-Tropsch synthesis in small amounts by cobalt catalysts and in larger amounts by iron catalysts at

moderate and high pressures. One may ask whether the synthesis of hydrocarbons can occur by the formation and subsequent dehydration of ethanol and higher alcohols. The data of Table 8 indicate that the dehydration of ethanol and higher alcohols is thermodynamically possible at synthesis temperatures. The reverse reactions, hydration of olefins, are not possible.

TABLE 8. EQUILIBRIUM CONSTANTS FOR THE DEHYDRATION OF ALCOHOLS [a]

$$C_nH_{2n+1}OH = C_nH_{2n} + H_2O$$

	$\log_{10} K_{eq}$		
Alcohol	127°C	227°C	327°C
Ethanol	0.9469 [b]	1.9957 [b]	2.6676 [b]
	0.6604	1.8933	2.7200
Propanol-1	2.2035	3.2709	3.9912
Butanol-1	1.7610	2.9642	3.7816
Hexanol-1	2.3056	3.657	4.5954

[a] All equilibrium constants except part of the data for ethanol were calculated from approximate free-energy equations of R. R. Wenner, *Chem. Eng. Progress*, **45**, 194 (1949).

[b] From data summarized by R. N. Pease, *Equilibrium and Kinetics of Gas Reactions*, Princeton University Press, 1942, p 79.

STABILITY OF HYDROCARBON PRODUCTS

In this section the thermodynamics of reactions involving the hydrocarbon products of the synthesis will be considered. This discussion includes the thermodynamics of the decomposition of hydrocarbons to carbon and hydrogen, the relative stability of isomers, equilibrium constants for hydrogenation of olefins, and finally the possibility of formation of heavier hydrocarbons from lighter ones by polymerization or incorporation in the Fischer-Tropsch synthesis.

All hydrocarbons except methane and ethane are thermodynamically unstable with respect to decomposition to carbon and hydrogen at temperatures above 100°C, the free energy of formation of methane and ethane from the elements becoming positive at about 550° and 200°C, respectively.

The equilibrium constants for isomerization reactions of saturated and olefinic hydrocarbons usually do not differ from one by more than a factor of 10, as shown in Table 9. This table contains equilibrium constants for isomerization of *n*-pentane and *n*-hexane to corresponding branched-chain paraffins and for 1-pentene to branched C_5 olefins. Equilibrium constants for the hydrogenation of α-olefins are presented

Table 9. Equilibrium Constants for Isomerization Reactions [a]

	$\log_{10} K_{eq}$		
	127°C	227°C	327°C
	n-pentane = *x*-pentane		
2-Methyl butane	0.765	0.560	0.412
2,2-Dimethyl propane	0.366	−0.140	−0.470
	1-pentene = *x*-pentene		
cis-2-Pentene	0.840	0.597	0.427
trans-2-Pentene	1.137	0.833	0.631
2-Methyl-1-butene	1.712	1.293	1.018
3-Methyl-1-butene	0.297	0.122	0.049
2-Methyl-2-butene	2.338	1.729	1.317
	n-hexane = *x*-hexane		
2-Methyl pentane	0.541	0.342	0.208
3-Methyl pentane	0.219	0.106	0.037
2,2-Dimethyl butane	0.940	0.442	0.124
2,3-Dimethyl butane	0.257	−0.008	−0.178

[a] Computed from data of reference 7.

in Table 10. These constants are sufficiently high so that olefins in the Fischer-Tropsch products must be formed by a primary process and not by a subsequent dehydrogenation of paraffins. Similarly, straight-chain paraffins cannot be produced in sizable amounts by isomerization of branched paraffins, nor α-olefins from their isomers. The presence of chiefly straight-chain paraffins and large amounts of α-olefins indicates that these reaction products are formed by primary processes and not by isomerization.

Table 10. Equilibrium Constants for Hydrogenation of Olefins [a, b]

Reaction	$\log_{10} K_{eq}$		
	27°C	227°C	427°C
$C_2H_4 + H_2 = C_2H_6$	17.549	7.901	3.678
$C_3H_6 + H_2 = C_3H_8$	15.001	6.215	2.393
$C_4H_8 + H_2 = C_4H_{10}$	15.236	6.365	2.471
$C_6H_{12} + H_2 = C_6H_{14}$	15.075	6.225	2.343
$C_{10}H_{20} + H_2 = C_{10}H_{22}$	15.080	6.223	2.341

[a] Computed from data of reference 7.

[b] All data for hydrogenation of 1-olefin to *n*-paraffin.

We next consider reactions that may occur between hydrocarbons produced in the synthesis and (*a*) other hydrocarbons; (*b*) hydrogen, yielding methane and a lower saturated hydrocarbon; and (*c*) hydrogen

and carbon monoxide in the synthesis. Equilibrium constants for reactions between hydrocarbons are given in Table 11. Reactions 1–3 of this table show that the condensation of methane with saturated hydrocarbons cannot occur to an appreciable extent at any temperature used in the synthesis. Reactions of methane and olefins (reactions 4–6) are thermodynamically favorable up to at least 227°C. Reactions of ethylene with higher saturated hydrocarbons (reactions 7–9) are thermodynamically possible up to 390°C, and reactions between two olefin molecules (reactions 10 and 11) are possible up to temperatures higher than 400°C.

Table 11. Equilibrium Constants for Reactions between Hydrocarbons [a]

Reaction [b]	$\log_{10} K_{eq}$ 27°C	227°C	427°C	Temperature at Which $K_{eq} = 1$, °C
1. $CH_4 + C_2H_6 = C_3H_8 + H_2$	−10.453	−6.514	−4.709	427
2. $CH_4 + C_4H_{10} = C_5H_{12} + H_2$	−10.155	−6.357	−4.614	427
3. $CH_4 + C_8H_{18} = C_9H_{20} + H_2$	−10.341	−6.457	−4.684	427
4. $CH_4 + C_2H_4 = C_3H_8$	+ 7.096	+1.387	−1.032	325
5. $CH_4 + C_4H_8 = C_5H_{12}$	+ 5.081	+0.008	−2.143	228
6. $CH_4 + C_8H_{16} = C_9H_{20}$	+ 4.739	+0.233	−2.343	240
7. $C_2H_4 + C_2H_6 = C_4H_{10}$	+ 8.826	+2.424	−0.288	398
8. $C_2H_4 + C_4H_{10} = C_6H_{14}$	+ 9.040	+2.471	−0.300	398
9. $C_2H_4 + C_8H_{18} = C_{10}H_{22}$	+ 8.833	+2.353	−0.382	390
10. $2C_2H_4 = C_4H_8$	+11.139	+3.960	+0.919	521
11. $C_2H_4 + C_4H_8 = C_6H_{12}$	+ 9.202	+2.611	−0.172	410

[a] Computed from data of reference 7.

[b] All hydrocarbons in this table are *n*-paraffins or 1-olefins.

Hydrogenation of olefins (Table 10) is thermodynamically possible at all synthesis temperatures, and the hydrocracking of saturated hydrocarbons (the reverse of reactions 1–3 of Table 11) is also possible at all synthesis temperatures.

Table 12 presents data for reactions of hydrogen and carbon monoxide with methane or olefins to produce hydrocarbons. The temperature below which the incorporation of methane (by reactions 1–6) is thermodynamically possible is higher the greater the ratio of synthesis gas to methane consumed. The reactions producing saturated hydrocarbons are possible to higher temperatures than those forming olefins, the incorporation of methane to yield saturated hydrocarbons being possible up to about 350°C. The incorporation of olefins to produce saturated hydrocarbons is energetically possible up to at least 395°C,

and similar reactions that produce olefins are possible up to at least 376°C. The incorporation of methane or olefins by reactions in which carbon dioxide is the oxygenated product is thermodynamically possible up to temperatures about 50°C higher than by the corresponding reactions that yield water.

Table 12. Incorporation of Hydrocarbons into the Products of the Synthesis [a]

Reaction [b]	$\log_{10} K_{eq}$ 27°C	227°C	427°C	Temperature at Which $K_{eq} = 1$, °C
1. $CH_4 + 4H_2 + 2CO = C_3H_8 + 2H_2O$	26.935	6.241	− 2.875	349
2. $CH_4 + 3H_2 + 2CO = C_3H_6 + 2H_2O$	11.934	0.026	− 5.268	228
3. $CH_4 + 8H_2 + 4CO = C_5H_{12} + 4H_2O$	55.897	13.675	− 4.910	360
4. $CH_4 + 7H_2 + 4CO = C_5H_{10} + 4H_2O$	40.825	7.466	− 7.241	312
5. $CH_4 + 16H_2 + 8CO = C_9H_{20} + 8H_2O$	113.270	28.106	− 9.348	363
6. $CH_4 + 15H_2 + 8CO = C_9H_{18} + 8H_2O$	98.190	21.884	−11.689	341
7. $C_2H_4 + 5H_2 + 2CO = C_4H_{10} + 2H_2O$	46.214	15.179	+ 1.547	>427
8. $C_2H_4 + 4H_2 + 2CO = C_4H_8 + 2H_2O$	30.977	8.814	+ 0.924	>427
9. $C_2H_4 + 17H_2 + 8CO = C_{10}H_{22} + 8H_2O$	132.444	36.916	− 5.047	395
10. $C_2H_4 + 16H_2 + 8CO = C_{10}H_{20} + 8H_2O$	117.364	30.694	− 7.388	376
11. $C_4H_8 + 13H_2 + 6CO = C_{10}H_{22} + 6H_2O$	101.467	28.103	− 4.123	393
12. $C_4H_8 + 12H_2 + 6CO = C_{10}H_{20} + 6H_2O$	86.387	21.880	− 6.464	368

[a] Computed from data of reference 7.

[b] All hydrocarbons in this table are normal paraffins and 1-olefins.

Prettre [10] has considered the incorporation of methane in the Fischer-Tropsch process in more detail. Standard free-energy changes were computed for the general reactions

$$(n - x)CO + (2n + 1 - 3x)H_2 + xCH_4 = C_nH_{2n+2} + (n - x)H_2O \qquad (6A)$$

and

$$2(n - x)CO + (n + 1 - 2x)H_2 + xCH_4 = C_nH_{2n+2} + (n - x)CO_2 \qquad (6B)$$

and these data for various values of n and x are reproduced in Tables 13 and 14. At 227°C with water as the oxygenated product, the free-energy changes are negative until x is about 40 per cent of n. At the same temperature with carbon dioxide as the oxygenated product, the free-energy change is negative until x exceeds 50 per cent of n.

From approximate thermodynamic data, Wenner [11] estimated the equilibrium constants for the production of propionaldehyde and isobutyraldehyde by the oxo reaction, as shown by the following equation

[11] R. R. Wenner, *Chem. Eng. Progress*, **45**, 200 (1949).

for the formation of propionaldehyde:

$$C_2H_4 + H_2 + CO = C_2H_5CHO \qquad (7)$$

The estimated equilibrium constants for the production of propionaldehyde and isobutyraldehyde by the oxo reaction are 6×10^{12} and 2.5×10^9 at 25°C and 324 and 1.6 at 227°C, respectively. Thus, it appears that these reactions are thermodynamically feasible, even at atmospheric pressure, at temperatures at least as high as 200°C.

TABLE 13. THERMODYNAMICS OF THE INCORPORATION OF METHANE INTO THE FISCHER-TROPSCH SYNTHESIS BY REACTION 6A[a]

n	x	$\Delta H°$	$\Delta F°$						
			27°C	127°C	227°C	327°C	427°C	527°C	627°C
1	0	− 45.889	−33.873	−28.573	−23.018	−17.285	−11.437	− 5.512	+478
2	0	− 76.321	− 51.323	− 40.465	−29.180	−17.622	− 5.872	+ 5.988	...
	0.5	− 53.377	− 34.385	− 26.188	−17.673	− 8.979	− 0.154	+ 8.746	...
	1	− 30.432	− 17.450	− 11.908	− 6.166	− 0.336	+ 5.564	+11.504	...
	1.5	− 7.488	− 0.513	+ 2.370	.....	.....	.....	.....	...
3	0	−109.188	− 70.848	− 54.336	−37.202	−19.888	− 2.228	+15.552	...
	0.5	− 86.244	− 53.911	− 40.058	−25.695	−11.245	+ 3.490	+18.310	...
	1	− 63.299	− 36.975	− 25.779	−14.188	− 2.602	+ 9.208	+21.068	...
	1.5	− 40.355	− 20.037	− 11.501	− 2.681	+ 6.041	.....	.....	...
	2	− 17.410	− 3.101	+ 2.778	+ 8.826	.....	.....	.....	...
4	0	−142.940	− 90.671	− 68.601	−45.828	−22.594	+ 0.956	+24.636	...
	0.5	−119.996	− 73.734	− 54.323	−34.321	−13.951	+ 6.674	+27.394	...
	1	− 97.052	− 56.797	− 40.044	−22.814	− 5.308	+12.392	+30.152	...
	1.5	− 74.108	− 39.860	− 25.766	−11.307	+ 3.335	.....	.....	...
	2	− 51.163	− 22.923	− 11.487	+ 0.200	+11.978	.....	.....	...
	2.5	− 28.217	− 5.987	+ 2.791	.....	.....	.....	.....	...
	3	− 5.273	+ 10.950	.....	.....	.....	.....	.....	...
5	0	−176.780	−110.605	− 82.885	−54.300	−25.190	+ 4.290	+33.940	...
	0.5	−153.836	− 93.668	− 68.607	−42.793	−16.547	+10.008	.....	...
	1	−130.891	− 76.731	− 54.328	−31.286	− 7.904	+15.725	.....	...
	1.5	−107.947	− 59.794	− 40.050	−19.779	+ 0.739	+21.444	.....	...
	2	− 85.002	− 42.857	− 25.771	− 8.272	+ 9.382	.....	.....	...
	2.5	− 62.058	− 25.920	− 11.493	+ 3.235	+18.025	.....	.....	...
	3	− 39.113	− 8.983	+ 2.786	.....	.....	.....	.....	...
10	0	−344.690	−209.040	−153.080	−95.560	−37.070	+22.070	.....	...
	1	−298.801	−175.166	−124.523	−72.546	−19.784	+33.506	.....	...
	2	−252.912	−141.292	− 95.966	−49.532	− 2.498	+44.942	.....	...
	3	−207.023	−107.418	− 67.409	−26.518	+14.788	.....	.....	...
	4	−161.134	− 73.544	− 38.852	− 3.504	+32.074	.....	.....	...
	5	−115.255	− 39.670	− 10.295	+19.510	.....	.....	.....	...
	6	− 69.356	− 5.796	+ 18.262	.....	.....	.....	.....	...
	7	− 23.467	+ 18.078	.....	.....	.....	.....	.....	...

[a] Prettre; see reference 10.

TABLE 14. THERMODYNAMICS OF THE INCORPORATION OF METHANE INTO THE FISCHER-TROPSCH SYNTHESIS BY REACTION 6*B* [a]

n	*x*	$\Delta H°$	$\Delta F°$						
			27°C	127°C	227°C	327°C	427°C	527°C	627°C
1	0	− 55.552	− 40.672	− 34.376	− 27.863	−21.218	−14.497	− 7.732	−935
2	0	− 95.645	− 64.921	− 52.069	− 38.880	−25.486	−11.990	+ 1.150	...
	0.5	− 67.870	− 44.585	− 34.889	− 24.948	−14.877	− 4.742	+ 5.418	...
	1	− 40.095	− 24.249	− 17.710	− 11.016	− 4.268	+ 2.505	+ 9.285	...
	1.5	− 12.320	− 3.913	− 0.530	+ 2.916	.....	.....	.....	...
3	0	−138.177	− 91.245	− 71.740	− 51.752	−31.684	−11.405	+ 8.880	...
	0.5	−110.381	− 70.909	− 54.162	− 37.820	−21.075	− 4.157	+12.755	...
	1	− 82.625	− 50.572	− 37.383	− 23.888	−10.466	+ 3.090	+16.630	...
	1.5	− 54.849	− 30.236	− 20.202	− 9.956	+ 0.143	.....	.....	...
	2	− 27.073	− 9.899	− 3.024	+ 3.976	+10.752	.....	.....	...
4	0	−181.592	−117.867	− 91.809	− 65.228	−38.322	−11.280	+15.760	...
	0.5	−153.816	− 97.531	− 74.629	− 51.296	−27.713	− 4.032	+19.631	...
	1	−126.040	− 77.195	− 57.450	− 37.364	−17.104	+ 3.216	.....	...
	1.5	− 98.264	− 56.859	− 40.270	− 23.432	− 6.495	+10.465	.....	...
	2	− 70.488	− 36.523	− 23.091	− 9.500	+ 4.214	.....	.....	...
	2.5	− 42.712	− 16.187	− 5.911	+ 4.432	.....	.....	.....	...
5	0	−225.095	−144.600	−111.890	− 78.550	−44.850	−11.005	+22.845	...
	0.5	−197.319	−124.264	− 94.711	− 64.618	−34.241	− 3.757	+26.717	...
	1	−169.543	−103.927	− 77.532	− 50.686	−23.632	+ 3.490	.....	...
	1.5	−141.767	− 83.591	− 60.353	− 36.754	−13.023	+10.738	.....	...
	2	−113.991	− 63.254	− 43.174	− 22.822	− 2.414	+17.985	.....	...
	2.5	− 86.215	− 42.918	− 25.995	− 8.890	+ 8.195	.....	.....	...
	3	− 58.439	− 22.581	− 8.817	+ 5.042	+17.804	.....	.....	..
10	0	−441.320	−277.030	−211.300	−144.060	−76.390	− 8.520	+59.290	..
	1	−385.768	−236.357	−176.741	−116.196	−55.172	+ 5.975	.....	...
	2	−330.216	−195.684	−142.382	− 88.332	−33.954	+20.470	.....	...
	3	−274.664	−155.011	−108.023	− 60.468	−12.736	+34.965	.....	...
	4	−219.112	−114.338	− 73.664	− 32.604	+ 8.482	.....	.....	...
	5	−163.560	− 73.665	− 39.305	− 4.740	+29.700	.....	.....	...

[a] Prettre; see reference 10.

THERMODYNAMICS OF PROCESSES RELATED TO THE FISCHER-TROPSCH SYNTHESIS

The Water-Gas Equilibrium

Equilibrium constants for the water-gas reaction, $H_2 + CO_2 = H_2O + CO$, are given in Table 15. At temperatures below 800°C the equilibrium very much favors the formation of carbon dioxide and hydrogen. Thus, the formation of carbon dioxide from water vapor formed

in the synthesis is thermodynamically possible, and if water is found in the products, it is due to the slowness of the subsequent water-gas reaction.

TABLE 15. EQUILIBRIUM CONSTANTS FOR THE WATER-GAS REACTION

$$H_2 + CO_2 = CO + H_2O$$

$$K_{eq} = \frac{p_{CO} \times p_{H_2O}}{p_{H_2} \times p_{CO_2}}$$

Temperature, °C	K_{eq} [a]	K_{eq} [b]
127	6.90×10^{-4}	
227	7.71×10^{-3}	
327	3.71×10^{-2}	
427	0.11	
450		0.137
500		0.207
527	0.247	
600		0.380
627	0.451	
700		0.624
727	0.719	
800		0.917
827	1.04	

[a] L. S. Kassel, *J. Am. Chem. Soc.*, **56**, 1,838 (1934).
[b] P. H. Emmett and J. F. Shultz, *ibid.*, **52**, 4,268 (1930).

EQUILIBRIUM CONSTANTS FOR THE REDUCTION OF OXIDES OF IRON, COBALT, AND NICKEL WITH HYDROGEN OR CARBON MONOXIDE

The thermodynamics of the reduction of the oxides of iron, cobalt, and nickel is of importance to the study of the Fischer-Tropsch synthesis for two reasons: (*a*) all catalysts are reduced to some extent either before use in the synthesis or in early stages of the synthesis, and (*b*) with these data it is possible to predict the stable state of the bulk of the catalyst in the actual synthesis. Equilibrium constants for the reduction of oxides with hydrogen and carbon monoxide are given in Tables 16 and 17, respectively. The equilibrium constants for the reduction of iron oxide are of the order of 0.1 per cent of those of cobalt oxide and 0.01 per cent of those of nickel oxide. Ferrous oxide does not appear as a stable phase below 560°C. The reduction of ferric oxide to magnetite (for which no data are given) has higher equilibrium constants and occurs more readily than the reduction of magnetite to iron. Reduction of

oxides with carbon monoxide or synthesis gas may be complicated by the formation of free carbon and carbides.

The equilibrium constants for the reduction of cobalt and nickel oxides are sufficiently large so that metal is the stable bulk phase in

TABLE 16. EQUILIBRIUM CONSTANTS FOR THE REDUCTION OF IRON, COBALT, AND NICKEL OXIDES WITH HYDROGEN

	$K_{eq} = p_{H_2O}/p_{H_2}$			
Temperature, °C	Iron [a]		Cobalt [b]	Nickel [c]
	Reaction A		*Reaction D*	*Reaction E*
200	0.013 [d]		110 [d]	1,370 [d]
227	0.019 [d]		105 [d]	1,130 [d]
300	0.044 [d]		90 [d]	710 [d]
327	0.058 [d]		86 [d]	620 [d]
335			85	
400	0.107		78 [d]	440 [d]
427	0.129 [d]		72 [d]	402 [d]
450			67	
485				330
500	0.214			
515			57	
527	0.240		56 [d]	290 [d]
550	0.283			
	Reaction B	*Reaction C*		
570			50.5	
600	0.461	0.334		240
700	1.16	0.419		
800	2.35	0.501		

Reaction *A* $\frac{1}{4}Fe_3O_4 + H_2 = \frac{3}{4}Fe + H_2O$
Reaction *B* $Fe_3O_4 + H_2 = 3FeO + H_2O$
Reaction *C* $FeO + H_2 = Fe + H_2O$
Reaction *D* $CoO + H_2 = Co + H_2O$
Reaction *E* $NiO + H_2 = Ni + H_2O$

[a] P. H. Emmett and J. F. Shultz, *J. Am. Chem. Soc.*, **52**, 4,268 (1930); **55**, 1,376 (1933).

[b] P. H. Emmett and J. F. Shultz, *ibid.*, **51**, 3,249 (1929). There is a transition from hexagonal (α) to cubic (β) cobalt at 340°–360°C.

[c] R. N. Pease and R. S. Cook, *ibid.*, **48**, 1,199 (1926).

[d] Interpolated or extrapolated from experimental values.

equilibrium with the gases normally encountered in the synthesis. For iron catalysts the ratio of p_{H_2O}/p_{H_2} is usually sufficiently high in the synthesis so that magnetite should be the equilibrium phase, while the ratio of p_{CO_2}/p_{CO} is usually smaller than the equilibrium constant and

exceeds it only at high conversions. Synthesis gas containing only hydrogen and carbon monoxide is a good reducing agent for iron catalysts, but as the reactants are consumed and water vapor and carbon dioxide formed, the gas becomes an oxidizing agent.

Table 17. Equilibrium Constants for the Reduction of Iron, Cobalt, and Nickel Oxides with Carbon Monoxide

	$K_{eq} = p_{CO_2}/p_{CO}$[a]		
Temperature, °C	Iron *Reaction A'*	Cobalt *Reaction D'*	Nickel *Reaction E'*
227	2.46	1.36×10^4	1.46×10^5
327	1.56	2.32×10^3	1.67×10^4
427	1.16	6.48×10^2	3.62×10^3
450		4.89×10^2 [b]	
527	0.97	2.27×10^2	1.17×10^3
570		1.48×10^2 [b]	

Reaction A' $\frac{1}{4}Fe_3O_4 + CO = \frac{3}{4}Fe + CO_2$
Reaction D' $CoO + CO = Co + CO_2$
Reaction E' $NiO + CO = Ni + CO_2$

[a] All data calculated from data in Tables 15 and 16 except those marked [b].
[b] P. H. Emmett and J. F. Shultz, *J. Am. Chem. Soc.*, **52**, 1,782 (1930).

The thermodynamics of the surface layers of atoms may be considerably different from those of the bulk-phase material. Almquist and Black [12] and Brunauer and Emmett [13] found that surface oxide was formed on iron catalysts at ratios of p_{H_2O}/p_{H_2} 1,000 times smaller than that required to form bulk-phase oxide. Thus, iron Fischer-Tropsch catalysts certainly have sizable amounts of surface oxide, and it is also possible that cobalt and nickel catalysts have oxidized surfaces.

Thermodynamics of Carbides of Iron

Three carbides of iron are of interest in the Fischer-Tropsch synthesis: hexagonal Fe_2C, Hägg Fe_2C, and cementite Fe_3C. Between 300° and 400°C, or possibly at even lower temperatures, the hexagonal carbide decomposes to Hägg carbide, which in turn decomposes to cementite. Thus, the carbides and metal may be arranged in the order of increasing stability as

Fe_2C (hexagonal), Fe_2C (Hägg), Fe_3C (cementite), and α-Fe

[12] J. A. Almquist and C. A. Black, *J. Am. Chem. Soc.*, **48**, 2,814 (1926).
[13] S. Brunauer and P. H. Emmett, *ibid.*, **52**, 2,682 (1930).

Emmett and coworkers [14] determined the free energies of formation of cementite and Fe_2C (Hägg), these data being presented in Tables 18 and 19. Enthalpies of formation of cementite are included in the data of Table 18, as well as comparison of free energies and enthalpies of formation with those of Watase.[15] Both cementite and Fe_2C (Hägg) have

TABLE 18. FREE ENERGIES AND ENTHALPIES OF FORMATION OF CEMENTITE

$$3Fe_\alpha + C_g = Fe_3C$$

Temperature, °C	$\Delta F°$, kcal		ΔH, kcal	
	a	*b*	*a*	*b*
0	+4.661	+4.487	+5.756	+5.448
127	4.174	4.043	6.428	6.120
227	3.542	3.461	6.742	6.434
327	2.93	2.82	6.839	6.531
427	2.32	2.16	6.781	6.473
523	1.64	1.51	6.438	6.206

[a] Watase; see reference 15.

[b] Emmett and coworkers; see reference 14.

TABLE 19. FREE ENERGIES OF FORMATION OF Fe_2C (HÄGG)

$$2Fe_\alpha + C_g = Fe_2C \text{ (Hägg)} [a]$$

Temperature, °C	$\Delta F°$, kcal
177	+3.866
227	3.821
327	3.458
377	3.140

[a] Emmett and coworkers; see reference 14.

positive free energies of formation which become less positive with increasing temperature. Computation of the standard-state free-energy changes for the formation of these carbides by the reactions

$$3Fe + 2CO = Fe_3C + CO_2 \quad (8)$$

$$2Fe + 2CO = Fe_2C \text{ (Hägg)} + CO_2 \quad (9)$$

resulted in the values -16.57 and -12.91 kcal for reaction 8 and -16.20 and -12.27 kcal for reaction 9 at 227° and 327°C, respectively.

[14] J. T. Kummer, L. C. Browning, and P. H. Emmett, *J. Chem. Phys.*, **16**, 740 (1948); L. C. Browning, T. W. DeWitt, and P. H. Emmett, *J. Am. Chem. Soc.*, **72**, 4,211 (1950).

[15] T. Watase, *J. Chem. Soc. Japan*, **54**, 110 (1933); *Z. physik. Chem.*, **147A**, 390 (1930).

Emmett and coworkers [14] computed equilibrium constants for the reduction of these carbides to paraffinic and olefinic hydrocarbons, as presented in Table 20. The data indicate that bulk-phase Fe_2C can be hydrogenated to paraffins of chain length shorter than C_5 at 227°C, while at 327°C only methane and ethane can be produced. Olefinic hydrocarbons cannot be produced in appreciable amounts at any of

Table 20. Equilibrium Constants for Hydrogenation of Fe_2C (Hägg) [a]

A. $nFe_2C + (n+1)H_2 = C_nH_{2n+2} + 2nFe$

B. $nFe_2C + nH_2 = C_nH_{2n} + 2nFe$

Temperature, °C	n	log K_p Paraffins *Reaction A*	log K_p Olefins *Reaction B*
177	2	+ 4.827	− 5.19
	4	2.580	− 5.28
	6	0.93	− 6.80
	8	− 0.85	
227	2	+ 2.829	− 5.07
	4	0.184	− 6.19
	6	− 2.421	− 8.65
	8	− 5.136	
327	2	+ 0.339	− 5.11
	4	− 3.933	− 8.03
	6	− 8.190	−12.16
	8	−12.58	
377	2		− 5.22
	4		− 8.94
	6		−14.02
427	2	− 0.67	
	4	− 5.71	
	6	−10.52	
	8	−15.77	

[a] Emmett and coworkers, reference 14.

the temperatures considered. The authors suggested that Fe_2C (hexagonal) would probably have similar free energies to the Hägg carbide and hence could not be hydrogenated to olefins and long-chain paraffins. Cementite is more stable than the Hägg carbide, and equilibrium constants for its hydrogenation to higher paraffins and olefins would be less favorable than those in Table 20. It should be noted that reaction of paraffin hydrocarbons above C_4 and olefins with iron is a possible method of converting a catalyst to Hägg carbide. The data above preclude the

direct hydrogenation of bulk-phase carbides of iron as a step in the Fischer-Tropsch synthesis. However, it is thermodynamically possible to incorporate one or more atoms of carbidic carbon with several carbon atoms from the reaction of hydrogen and carbon monoxide to form a hydrocarbon molecule, because the large negative free-energy change for the reaction of hydrogen and carbon monoxide is sufficient to make the net free-energy change negative.

Thermodynamic Data of Volatile Metal Carbonyls

Metal carbonyls are of considerable interest because removal of active metal from catalysts by carbonyl formation is probably one of the factors limiting the Fischer-Tropsch synthesis to relatively low pressures, as compared with the alcohol synthesis. Also, carbonyls may possibly be intermediates in the synthesis of hydrocarbons. In Table 21 are listed the melting points and decomposition temperatures at atmospheric pressure of volatile carbonyls and hydrocarbonyls of iron,

Table 21. Melting Points and Decomposition Temperatures of Volatile Metal Carbonyls and Hydrocarbonyls [a]

Carbonyl	Melting Point, °C	Decomposition Temperature, °C
$Ni(CO)_4$	−25	60
$[Co(CO_4)]_2$	50	53
$Fe(CO)_5$	−21	150
$Ru(CO)_5$	−22	− 15
$Co(CO)_4H$	−33	− 33
$Fe(CO)_4H_2$	−70	< − 33

[a] A. A. Blanchard, *Chem. Revs.*, **21**, 1 (1937).

cobalt, nickel, and ruthenium. The table does not include a number of known carbonyls, such as $Fe_2(CO)_9$, having considerably higher melting points. The carbonyls and hydrocarbonyls in Table 21 decompose at atmospheric pressure at relatively low temperatures. The equilibrium concentration of volatile carbonyls increases with partial pressure of carbon monoxide and decreases with temperature. Table 22 presents the equilibrium constants for iron carbonyl, and Figure 5 shows the equilibrium percentages of the carbonyl as a function of temperature and pressure.[16] The solid curves, G_1–G_5, show the equilibrium percentages of iron carbonyl vapor in carbon monoxide at various temperatures and

[16] H. Pichler and H. Walenda, *Brennstoff-Chem.*, **21**, 133 (1940).

pressures. Dotted curves D_1–D_4 represent the percentage of carbonyl corresponding to saturated carbonyl vapor. The intersections of the D and G curves I–IV and the line drawn between these points represent the greatest concentration of carbonyl that can be found in the gas

TABLE 22. FORMATION OF IRON PENTACARBONYL [a]

$$Fe + 5CO = Fe(CO)_5$$

$$\Delta H = -54.0 \text{ kcal per mole}$$

Temperature, °C	$\log_{10} K_p$	Temperature, °C	$\log_{10} K_p$
100	−3.53	250	−11.38
150	−6.77	300	−13.06
200	−9.32	350	−14.48

[a] H. Pichler and H. Walenda, reference 16.

phase, because at this line the pressure of the carbonyl is equal to its vapor pressure and any additional carbonyl will appear as liquid. The sharp vertical break in this curve occurs at the critical temperature of the carbonyl. With iron catalysts tested at 200° and 300°C and 10 atm

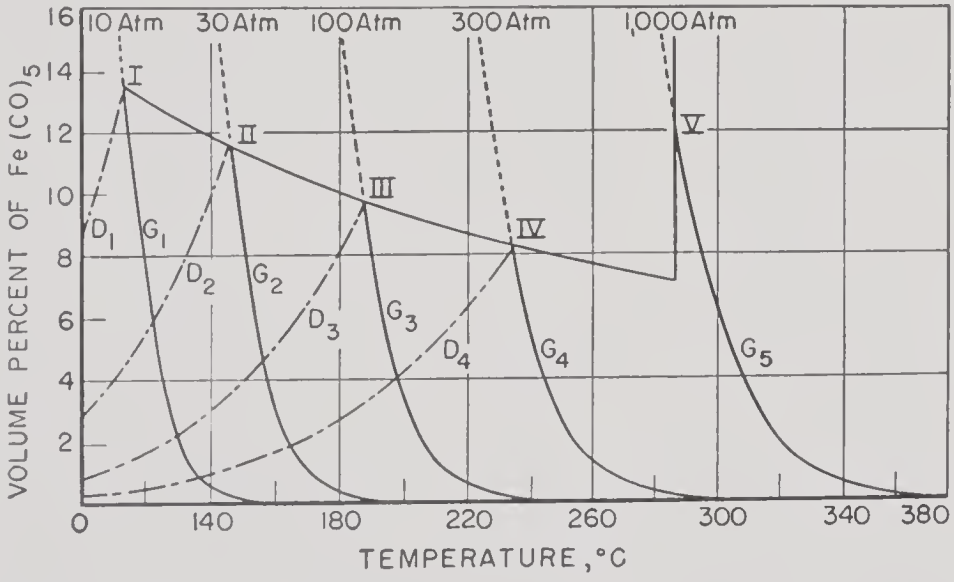


FIGURE 1–5. Equilibrium concentrations of $Fe(CO)_5$ at different pressures and temperatures. Reproduced from reference 16.

of $1H_2 + 1CO$ gas, the equilibrium concentrations of iron carbonyl are 10^{-5} and 10^{-8} volume per cent, respectively.

Mittasch [17] determined the equilibrium constants for the formation of nickel tetracarbonyl. These data, converted to K_{eq} in atmospheres,

[17] A. Mittasch, *Z. physik. Chem.*, **40**, 1 (1902).

are given in Table 23. These constants are about 1,000 times greater than those of iron pentacarbonyl. The equilibrium constants of both iron and nickel carbonyl are very dependent upon temperature.

TABLE 23. FORMATION OF NICKEL CARBONYL [a]

$$Ni + 4CO = Ni(CO)_4$$

Temperature, °C	$\log_{10} K_p$
20	3.70
30	2.92
50	1.60
70	0.42
90	−0.81

[a] A. Mittasch, reference 17.

An Introduction to Heterogeneous Catalysis

CHAPTER

2

General Considerations and Definitions

This chapter presents a review of heterogeneous catalysis. It is not an exhaustive or complete survey of the subject but is designed to acquaint the chemist and chemical engineer with modern methods and concepts of catalysis. Where possible, metal or metal oxide catalysts similar or identical to those used in the Fischer-Tropsch synthesis have been selected as examples. The chapter also contains a brief discussion of three catalytic reactions: the hydrogenation of olefins, the ammonia synthesis, and the synthesis of alcohols.

A catalyst may be defined as a substance that accelerates the rate at which a chemical reaction approaches equilibrium, the catalyst remaining relatively unchanged. When several reactions are thermodynamically possible, the nature of the catalyst and the operating conditions determine the course of the reaction. Any reaction that occurs must be accompanied by a negative free-energy change, but the reaction does not necessarily yield the products that are the most stable thermodynamically. Although the formation of methane from hydrogen and carbon monoxide at 300°C is accompanied by the greatest negative free change, methanol is produced on zinc chromite and similar oxide catalysts, and mixtures of paraffinic and olefinic hydrocarbons are produced on iron, cobalt, nickel, and ruthenium catalysts. The term "selectivity" is used to describe the ability of a catalyst to produce a given set of products in a system where other products are also thermodynamically possible.

The term "promoter" is defined as a substance added to a catalyst to improve its activity or specificity for a given reaction. Promoters may or may not be active in the reaction by themselves and usually are present in relatively small amounts. In most cases when two or more active components are present in nearly equal amounts, the term "mixed catalyst" is used. Promoters may be divided into two classes.

Structural promoters. These substances facilitate the formation of a structure of high surface area during the preparation or pretreatment of the catalyst and stabilize such a structure during use of the catalyst. Thus, reduced iron synthetic-ammonia catalysts promoted with small amounts of alumina have surface areas of 10–15 sq m per g, whereas similar preparations of reduced pure magnetite have areas less than 1 sq m per g.[1] Similarly, reduced cobalt-thoria catalysts have areas of about 15 sq m per g, and similar preparations of pure cobalt about 3 sq m per g.[2]

Chemical promoters. These substances change the chemical nature of the surface, thereby increasing the activity or selectivity of the catalyst. They may or may not cause an increase in, or stabilization of, surface area. For example, potassium oxide in doubly promoted synthetic-ammonia catalysts has little influence on surface area, nor does it have any great influence on activity in moderate-pressure operation (30 atm). However, this alkali increases considerably the catalytic activity at higher pressures (100 atm). It has been suggested that the alkali accelerates the desorption of ammonia, thus preventing its accumulation in amounts sufficient to inhibit the reaction in the higher-pressure operation.[3] In the Fischer-Tropsch synthesis with iron catalysts, small amounts of potassium carbonate cause marked changes in activity and product distribution. At the same temperature of testing, average molecular weight of the products increases with the amount of potassium carbonate at least up to about 2 parts per 100 Fe. The activity increases with alkali content up to about 0.5 part per 100 Fe, remains constant from 0.5 to 1.0 part per 100 Fe, and decreases with higher alkali content. In this class of promoters may be included those that accelerate the pretreatment of catalysts. For example, copper is added to precipitated cobalt or iron catalysts to accelerate the rate of pretreatment—reduction and/or carburization in hydrogen, carbon monoxide, or gases containing both—so that these catalysts may be pretreated at considerably lower temperatures. The presence of copper in amounts up to 20 parts per 100 Fe in iron catalysts has no great effect on either activity or product distribution, but with cobalt catalysts the copper is deleterious to the life of the catalyst.[4]

Carriers were originally introduced to dilute the active components

[1] S. Brunauer and P. H. Emmett, *J. Am. Chem. Soc.*, **59**, 2,682 (1937).

[2] R. B. Anderson, W. K. Hall, and L. J. E. Hofer, *ibid.*, **70**, 2,465 (1948).

[3] P. H. Emmett in *Twelfth Report of the Committee on Catalysis, National Research Council*, John Wiley & Sons, 1940, p 139.

[4] H. Pichler, Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen, *U. S. Bur. Mines Spec. Rept.*, 1947.

and increase the bulk volumes of catalysts containing expensive metals such as platinum. Although carriers were at first believed to be inert, in some cases there appears to be definite interaction between the carrier and the catalytically active substance which may at least in part be responsible for the enhanced activity of the supported catalyst. Visser and deLange [5] have shown that nickel hydrosilicate bonds are formed in nickel oxide-kieselguhr catalysts. Similar interaction may occur to a limited extent in cobalt Fischer-Tropsch catalysts.[2,6] Perhaps the most important function of carriers is to provide desirable distribution of pores and a suitable bulk density of the catalyst. Some carriers act like structural promoters in preventing excessive sintering of the active component. Commonly used carriers include kieselguhr, pumice, infusorial earth, asbestos, porous granules of silica or alumina, and a large number of other relatively inert porous solids. We shall include in this classification binding agents which act to cement fine powders or granules of low mechanical strength into particles sufficiently hard for use in catalytic processes.

Catalyst Development and Methods of Preparation

Theories of catalysis have not developed sufficiently so that a catalyst for a given reaction may be designed from a consideration of only the bulk-phase chemical and physical properties of the constituents. Certainly these data are helpful, but almost every successful catalyst has been developed by the trial and error method. This involves both direct experimentation and reference to similar experiments recorded in the literature. At present there exists a large body of data on various properties of catalysts and catalytic reactions. From similarities of catalytic reactions and properties of catalysts, periodic law, and other relationships between bulk properties of substances, it is possible to direct the search for catalysts into paths of probable success. The development of most catalysts used in industrial processes, including those for the Fischer-Tropsch synthesis, has followed the trial and error method.

Since catalytic reactions occur at the surface of the catalyst, it is necessary that the catalyst as used in the reaction have a moderately high surface area which is accessible to the reactants. Thus, the method of preparation should produce a catalyst that, after suitable pretreatment, has an active surface with a moderately high and accessible area. The

[5] G. H. Visser and J. J. deLange, *Ingenieur (Utrecht)*, **58**, 24 (1946).

[6] R. B. Anderson, A. Krieg, B. Seligman, and W. Tarn, *Ind. Eng. Chem.*, **40**, 2,347 (1948).

pretreated catalyst should also have sufficient mechanical strength and stability so that the particles will remain relatively unchanged during their use as catalysts. The requirements of activity and mechanical strength will vary considerably, depending upon the catalytic reaction and the type of reactor in which the catalyst is employed.

The methods of preparation of metal or metal oxide catalysts for the Fischer-Tropsch synthesis are described in detail in Chapter 3. They are:

Precipitated catalysts. The hydroxide, hydrous oxide, or basic carbonate is precipitated from an aqueous solution of the active constituent and promoters. If carriers are used, they may be added before or during the precipitation or may be merely mixed with the moist precipitate. The precipitate is then filtered, washed on the filter, and dried. Many hydrous oxides or basic carbonates are voluminous and/or gelatinous, and filtration and washing may be difficult. The method and extent of washing depend upon the sensitivity of the catalyst to adsorbed ions. If a carrier is used, the order of addition must be established by catalyst tests. Precipitated catalysts vary considerably in strength from soft powders to hard glassy gels.

Decomposition catalysts. Metal nitrates, oxalates, or other compounds mixed with promoters, if desired, are decomposed to metal oxides or metals by heating. The product is a fine powder; if rigid granules are desired, it is necessary to pellet this material or to cement it with a binding agent.

Impregnated catalysts. Solutions of metal nitrates or other soluble, easily decomposed salts of the metal and the promoters, if desired, are used to impregnate porous granules of relatively inert material. The impregnated granule is then heated to decompose the metal salt. The mechanical strength of the catalyst is usually equal to that of the porous granule.

Skeletal catalysts. An alloy of the active metal and, for example, aluminum or silicon is prepared by fusion. The aluminum or silicon is leached out with a solution of sodium or potassium hydroxide, leaving a skeleton of the active metal. These catalysts have sufficient mechanical strength for most processes.

Fused catalysts. These catalysts are prepared by fusing a mixture of the oxides of the active metal and promoters. The melt is crushed to give granules of the desired size. The granules have extremely low surface areas; however, on reduction the surface area increases to 5–15 sq m per g. These catalysts have high mechanical strength.

Cemented catalysts. Oxide powders, such as are prepared by precipitation or decomposition methods or inexpensive natural oxide ores,

may be shaped into usable granules by impregnation with suitable binders and promoters.

Powdered catalysts. Powdered oxides suitable for processes in which the catalyst is suspended in flowing gas or liquid may be prepared by heating natural oxide ores, by oxidation of sulfide ores, or by several of the previous methods.

Methods of Studying Catalysts

CHEMICAL ANALYSIS

Accurate analytical data are necessary in any systematic study of catalysts. It is usually impossible to predict catalyst composition from ratios of materials used in the preparation. First, the compounds in the finished catalyst may not be known or may be of variable composition. Thus, cobalt in precipitated catalysts is present as a basic carbonate of variable composition. Iron in precipitated catalysts is present as hydrous oxide containing variable amounts of water, and if the solution used in the preparation contains ferrous iron, the oxidation state of the iron may be variable. Iron in fused and highly sintered catalysts only approximates Fe_3O_4, the catalyst having widely varying ratios of ferric to ferrous iron. Second, steps in the preparation may not be quantitative because of incomplete precipitation or volatilization of some components in fusion or high-temperature sintering. Some catalysts are poisoned by traces of impurities, and thus both the starting materials and finished catalyst as well as reactants must be free of these poisons. Chemical analysis is also valuable in following changes in the catalyst during pretreatment and use and can provide information about the average state of oxidation, carbon deposition, accumulation of products or poisons, and removal of active components.

X-RAY DIFFRACTION METHODS

X-ray diffraction data provide information as to the identity and amount of the various crystalline phases of the catalysts, as well as information about the size of and order in crystallites, interplanar spacings, and in some cases crystal structure, etc. Catalysts usually are studied by powder diffraction techniques, and samples of reduced or used catalysts for x-ray examination may be easily prepared without contamination with air. Phase identification may be made by comparison with the powder patterns of known pure substances or with published patterns of pure substances such as those compiled in the Hanawalt index

cards of x-ray reflections.[7] Thus, it is possible to identify the phases present in raw, reduced, and used catalysts, and to follow changes in these phases during pretreatment or use in the catalytic reaction.

Quantitative analysis of catalysts by x-ray diffraction methods is neither simple nor very accurate for several reasons: (*a*) background scattering (instrumental and various types of disorder in the crystallites), (*b*) line broadening, (*c*) differences in the reflections from various phases due to the difference of scattering power of the constituent atoms, (*d*) differences in reflection intensities due to the size of the unit cell and degree of symmetry, (*e*) accidental interference of lines, and (*f*) fluorescent radiation from the sample and difficulties inherent in methods of measuring intensity of lines. The use of a highly crystalline internal standard with diffraction lines adjacent to lines of the phase to be determined eliminates some of the uncertainties. The amount of scattered x-radiation produced by a given phase (corrected for the various effects listed above) is a linear function of its concentration, but the extent to which the scattered radiation is diffracted into a discrete pattern is a function of the size and degree of ordering of the crystallites. Large crystallites give sharp, intense diffraction lines, whereas small crystallites produce broad, diffuse lines. In some cases substances with very small crystallites, such as amorphous ferric oxide gels, give very broad diffraction lines that can hardly be distinguished from the background of randomly reflected x-radiation.[8] Because many catalysts are prepared by methods that form a relatively amorphous, high-surface-area structure, their diffraction patterns are weak and diffuse, and even the identification of the phases present may be difficult. A mixture of a small amount of crystalline material with a large amount of nearly amorphous material may give only the diffraction pattern of the crystalline material. The intensity of the diffraction lines increases with the atomic number of the atoms involved. In used Fischer-Tropsch catalysts of iron, cobalt, or nickel, lines characteristic of carbon cannot usually be distinguished even though it may be present in sizable amounts. However, carbon present as carbides can be identified since the spacing between reflecting planes of metal atoms of the carbides is usually different from that of the metal. In view of these factors, it usually is impossible to identify phases present in quantities less than 5 per cent unless they exist in well-formed microscopic crystals; at best the accuracy of quantitative estimation is about ±3–5 per cent.

[7] American Society for Testing Materials, *Data Cards for Identification of Crystalline Materials*, Philadelphia, Pa.

[8] H. B. Weiser and W. O. Milligan, *Advances in Colloid Science*, vol. 1, Interscience Press, New York, 1942, p 227.

A fundamental limitation of the x-ray diffraction method is that it gives information only about the bulk-phase constituents of the catalyst. Since the catalytic properties of the material depend on the composition and structure of the surface, the information of x-ray diffraction is directly applicable only to the extent that the bulk-phase structure influences the nature of the surface.

One of the early x-ray studies of catalysts was that of Wyckoff and Crittenden on synthetic-ammonia catalysts.[9] They showed that the lattice spacings of magnetite and α-iron in unreduced and reduced fused Fe_3O_4-Al_2O_3-K_2O catalysts were the same as in normal magnetite and α-iron, respectively. An excess of ferrous iron caused the separation of ferrous oxide as a distinct phase. However, if an equivalent amount of alumina was added to the melted catalyst, the ferrous oxide phase disappeared with the formation of ferrous aluminate, which is isomorphous and forms a solid solution with magnetite. The x-ray patterns of the unreduced catalysts were sharp. Those of reduced catalysts were broad, indicating the presence of small crystallites. Reduced catalysts containing alumina gave broader diffraction lines than reduced pure magnetite. The resistance to sintering of the catalysts containing alumina was attributed to the effectiveness of uniformly dispersed alumina in preventing formation of large crystals. This was reflected in the mechanical properties of the catalysts: reduced pure magnetite was malleable, but a reduced catalyst promoted with alumina was brittle.

By x-ray diffraction methods, Weller, Hofer, and Anderson [10] showed that the bulk-phase carbide, Co_2C, was not an intermediate in the Fischer-Tropsch synthesis over cobalt catalysts. Catalysts used in the synthesis gave the same powder diffraction pattern as freshly reduced catalysts, namely, the pattern of disordered cobalt, and showed no evidence of cobalt carbide. Catalysts carburized in carbon monoxide gave the pattern of Co_2C. When the carbide was removed by hydrogenation at 200°C, the diffraction pattern of α-Co, rather than that of disordered cobalt, was found. Since the used catalyst showed only the disordered cobalt pattern, it was concluded that bulk-phase Co_2C had never been present in the catalyst. The data do not preclude the possibility that cobalt carbide present in a few layers at the catalyst surface may be an intermediate in the synthesis.

X-ray studies of iron synthetic-ammonia [9] and cobalt Fischer-Tropsch catalysts [11] have shown no very large alterations of lattice parameters of active components as compared with those of the bulk-

[9] R. W. G. Wyckoff and E. D. Crittenden, *J. Am. Chem. Soc.*, **47**, 2,866 (1925).
[10] S. Weller, L. J. E. Hofer, and R. B. Anderson, *ibid.*, **70**, 799 (1948).
[11] L. J. E. Hofer and W. C. Peebles, *ibid.*, **69**, 893, 2,497 (1947).

phase materials. However, for catalysts in which solid solution or compound formation occurs, considerable alteration of the lattice parameters has been observed (see this chapter, p 99, work of Frohlich).

In determining average crystallite size from line broadening, the following equation is usually used:

$$\beta = \frac{k\lambda}{d \cos \theta} \tag{1}$$

where β is the line breadth usually measured at half maximum intensity, λ is the wave length of x-rays used, θ is the Bragg angle of the line, d is the crystallite diameter, and k is a constant about equal to one. The breadth of the diffraction line β may be defined by $\sqrt{B_m^2 - B_s^2}$, where B_m and B_s are the breadths at half maximum intensity of the diffraction line of the sample being studied and of a nearby line of a standard substance known to have crystallites larger than 1,000 Å in diameter, respectively.[12] It should be noted that these are average diameters of crystallites and may or may not be the same as average particle diameters. This is illustrated in Table 1 by data of Alexander and Kummer,[13] in which average crystallite size determined by the line broadening

Table 1. Comparison of Average Crystallite Size from X-Ray Line Broadening with Average Particle Size from Gas Adsorption

	Line Broadening Method Av Crystallite Size, Å	Gas Adsorption Method Av Particle Size, Å
MgO heated at 600°C	140	220
MgO heated at 900°C	395	1,576
Ni catalyst	57	122
Fe from iron carbonyl	70	21,000 [a]

[a] Average particle size by microscopic examination, 25,000 Å.

method was compared with average particle size from surface areas determined by the gas adsorption method. It appears that the particles of magnesia heated at 900°C and the iron from carbonyl contain many crystallites. In all cases the crystallite size was smaller than the particle size. The methods of estimation of crystallite size from line broadening have been discussed by Birks and Friedman.[14]

Recently, studies of the scattering of x-rays at small angles from the incident beam have been used in determining the size of particles in catalysts. The small-angle diffraction is caused by the larger spacings

[12] B. E. Warren, *J. Applied Phys.*, **12**, 375 (1941).
[13] L. Alexander and E. Kummer, *ibid.*, to be published.
[14] L. S. Birks and H. Friedman, *ibid.*, **17**, 687 (1947).

in the catalysts, and this has been related to the particle size and pore distribution. Although at present the method is somewhat difficult and the interpretation of the data is possibly uncertain, in several instances remarkably good agreement has been found with average particle size and surface area predicted by the gas adsorption method.[15]

ELECTRON DIFFRACTION AND MICROSCOPY

In 1925, deBroglie [16] suggested that electrons and other particles have wave properties as defined by the equation $\lambda = h/p$, where λ is the wave length of the particle, p its momentum, and h Planck's constant. In 1926, Davisson and Germer [17] and Thomson and Reid [18] demonstrated that electrons are reflected from the surfaces of crystals in a manner similar to x-rays. Thin metal foils produced electron diffraction patterns similar to those of x-ray diagrams. The wave length from electron waves in angstrom units is given by $\lambda = 150.04/V$, where V is the accelerating potential in volts. Electron diffraction patterns are similar to corresponding x-ray diffraction patterns, and the lattice spacings calculated from the Bragg law are the same.

Since electron beams penetrate only very short distances, probably about 1,000 Å, electron diffraction is a method of studying the material near the surface of a catalyst. Extensive studies of evaporated films have been made by Finch,[19] Beeck,[20] and others. It is also possible to obtain electron diffraction patterns of finely crushed granules of catalysts, the pattern resulting from penetration and diffraction about the edges of the particles. In used Fischer-Tropsch catalysts [21] it is necessary to remove adsorbed hydrocarbons by solvent extraction; otherwise, the electron diffraction pattern will be that of the adsorbed hydrocarbon. In Figure 1 are shown electron diffraction patterns of a used iron Fischer-Tropsch catalyst before and after extraction in benzene. Diffraction pattern 1*a* corresponds to that of the adsorbed hydrocarbon, and pattern

[15] C. G. Shull and L. C. Roess, *ibid.*, **18,** 295 (1947); H. L. Ritter and L. C. Erich, *Anal. Chem.*, **20,** 665 (1948).

[16] L. deBroglie, *Phil. Mag.*, **47,** 446 (1924).

[17] C. Davisson and L. H. Germer, *Phys. Rev.*, **30,** 705 (1927).

[18] G. P. Thomson and A. Reid, *Proc. Roy. Soc.* (*London*) (*A*), **117,** 600 (1928); **119,** 651 (1928).

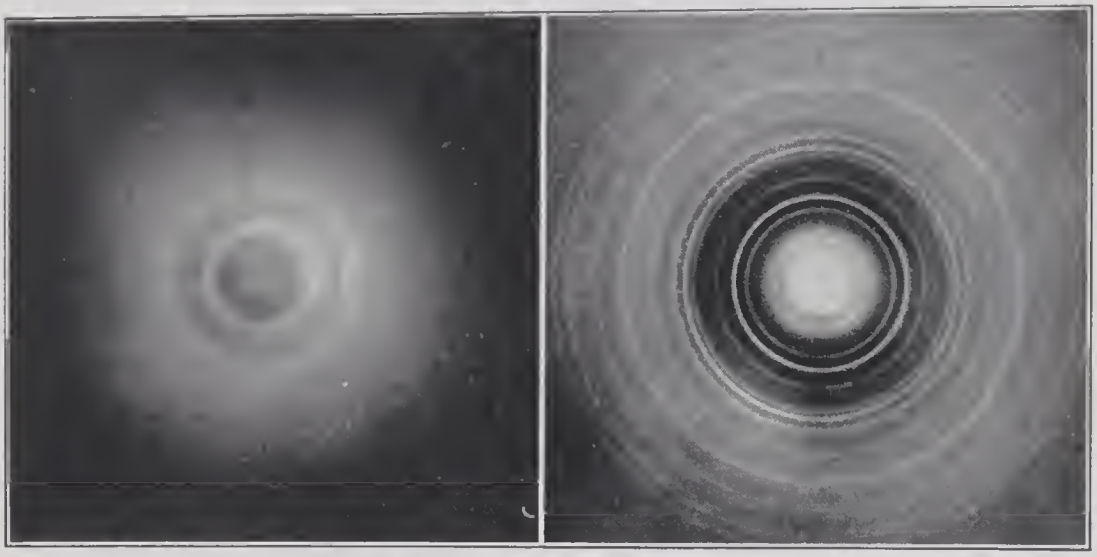
[19] G. I. Finch, *ibid.*, **141,** 414 (1933); **145,** 676 (1934); *Trans. Faraday Soc.*, **31,** 1051 (1935).

[20] O. Beeck, A. E. Smith, and A. Wheeler, *Proc. Roy. Soc.* (*London*) (*A*), **177,** 62 (1940).

[21] J. T. McCartney, R. B. Anderson, B. Seligman, and J. Lecky, Electron Diffraction Patterns of Fischer-Tropsch Catalysts, *J. Chem. Phys.*, to be published.

1*b* is that of magnetite. Particular care must be taken to prevent oxidation of metal catalysts in preparation and introduction of the sample into the diffraction apparatus.

The electron microscope has increased the range of magnification to greater than 100,000 diameters, these high magnifications being possible because of the short wave length of electrons. This instrument is excellent for examining submicroscopic powders, but some difficulty is experienced in handling granular catalysts. In some cases it is possible



(*a*) Before removal of wax. (*b*) After removal of wax.

FIGURE 2–1. Electron diffraction patterns of used iron catalysts: (*a*) diffraction pattern of adsorbed wax, and (*b*) diffraction pattern of Fe_3O_4. Unpublished U. S. Bureau of Mines data.

by gentle crushing to obtain particles fine enough for electromicroscopic examination without changing the structure of the catalyst too seriously.

Turkevich [22] and Shekter, Roginskii, and Isaev [23] have presented electron micrographs of various catalysts. Anderson, McCartney, Hall, and Hofer [24,25] have published micrographs of kieselguhrs as shown by Figure 2*a*, *b*, *c*, *d*, and *e* at magnifications of 2,000 and 20,000 diameters and have related the micrographs to surface areas and densities of the kieselguhrs. It is interesting to note that most of the fine structure evident at a magnification of 20,000 times is not apparent at 2,000.

[22] J. Turkevich, *ibid.*, **13**, 235 (1945).

[23] A. Shekter, S. Roginskii, and B. Isaev, *Acta Physicochim. U.R.S.S.*, **20**, 117 (1945).

[24] R. B. Anderson, J. T. McCartney, W. K. Hall, L. J. E. Hofer, *Ind. Eng. Chem.*, **39**, 1,618 (1947).

[25] H. H. Storch, R. B. Anderson, L. J. E. Hofer, C. O. Hawk, H. C. Anderson, and N. Golumbic, *U. S. Bur. Mines Tech. Paper* 709 (1948), 213 pp.

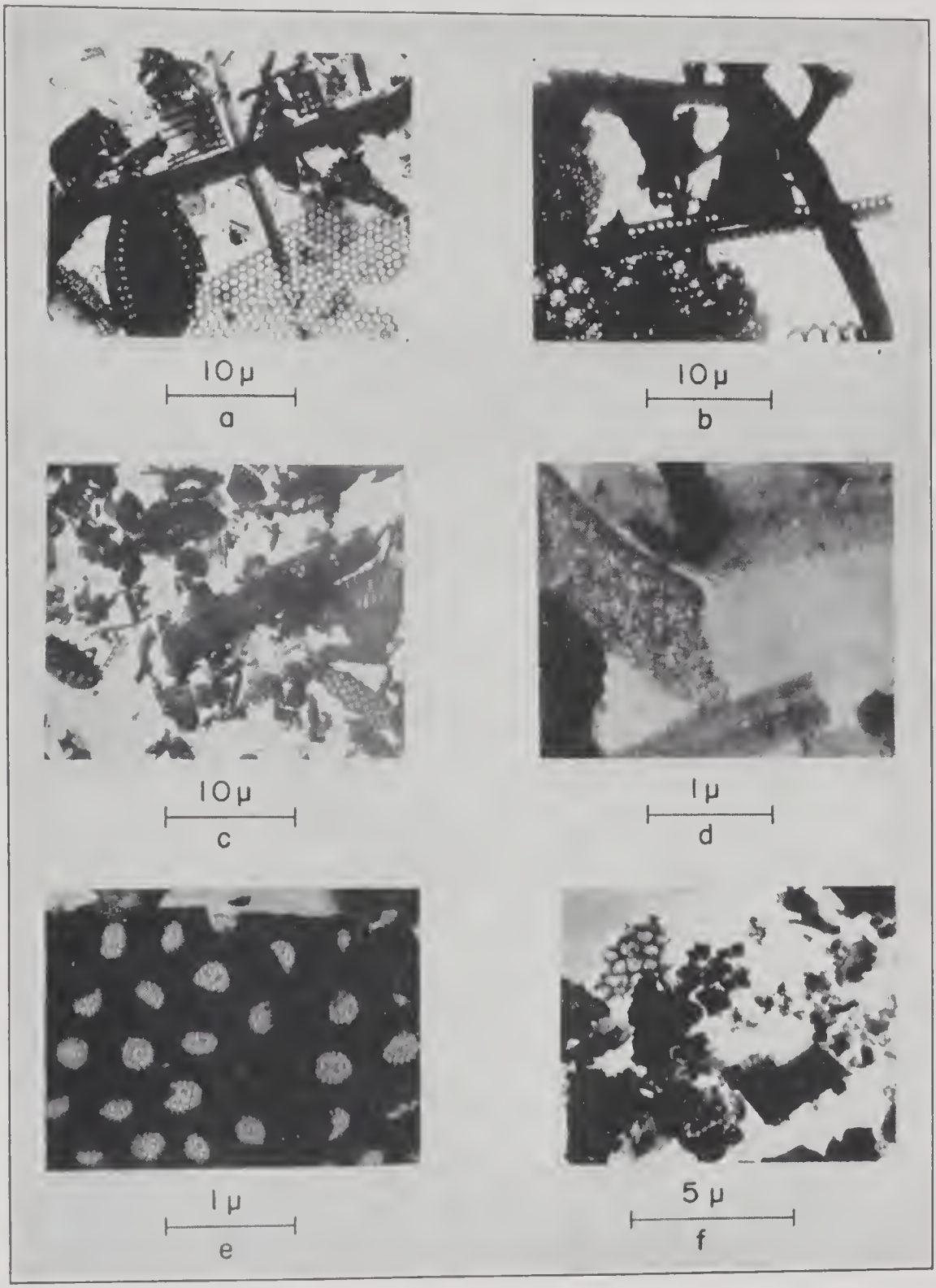


FIGURE 2–2. Electron micrographs of kieselguhrs and a cobalt Fischer-Tropsch catalyst: (*a*) Filter-Cel kieselguhr; (*b*) flux-calcined Hyflo Super-Cel; (*c*) and (*d*) Dicalite 911 kieselguhr; (*e*) German kieselguhr; and (*f*) cobalt-thoria-kieselguhr catalyst. Reproduced by permission from reference 24.

In Figure 2*f* is shown an electron micrograph of an unreduced cobalt-thoria-kieselguhr catalyst. The micrograph shows clusters of the cobalt basic carbonate-thoria complex covering and filling particles of kieselguhr; it also shows cobalt complex and kieselguhr particles which probably became separated in crushing the catalyst particle into a powder during preparation of the sample for microscopic examination. The outlines of the clumps of cobalt basic carbonate-thoria complex were feathery, indicating that the surface area of this part of the catalyst was considerably higher than that of the kieselguhr; this observation is in agreement with surface-area measurements by the gas adsorption method.

MAGNETIC METHODS

Usually no direct relationship exists between magnetic properties and catalytic activity. An important exception is the *para-* to *ortho*-hydrogen conversion which is catalyzed by para- or ferromagnetic surfaces as well as by atomic adsorption of hydrogen. The magnetic properties of catalysts may be used for qualitative and quantitative determination of phases present and for the determination of the structure of catalysts. Selwood [26] has reviewed the magnetic studies of catalysts. Only the thermomagnetic analysis of ferromagnetic components of catalysts will be described in this section.

Substances may be divided into three classes, based upon their behaviors in magnetic fields. In an inhomogeneous magnetic field a diamagnetic substance tends to move to the lowest-intensity portions of the field, while para- or ferromagnetic materials tend to move to the highest-intensity portions of the field. The force, F, on a substance in an inhomogeneous magnetic field, with a field gradient of dH/dx, is given by

$$F = m\sigma \frac{dH}{dx} = m\chi H \frac{dH}{dx} = M \frac{dH}{dx} \qquad (2)$$

where σ is the specific magnetization, m is the mass, χ the magnetic susceptibility ($\chi = \sigma/H$), and M the magnetic moment. The magnetic susceptibility of diamagnetic substances is independent of both temperature and field intensity; the magnetic susceptibility of paramagnetic materials varies inversely with temperature. Thus, for dia- and paramagnetic substances, the magnetic susceptibility is a useful quantity. The specific magnetization for ferromagnetic substances depends upon both field intensity and temperature in a complicated manner. When the field strength is increased from zero, the specific magnetization in-

[26] P. W. Selwood, *Chem. Revs.*, **38**, 41 (1946).

creases enormously and approaches a constant saturation value, σ_s, as the field strength is further increased. This saturation value is characteristic of the ferromagnetic material at a given temperature. When the field is decreased, the well-known hysteresis phenomenon is observed. Ferromagnetism is not an atomic property, but is a cooperative or "domain" effect due to the interaction of a group of atoms or molecules. The minimum size of a ferromagnetic particle has been determined to be 10–12 Å for iron [27] and 30–40 Å for γ-Fe_2O_3.[28] All ferromagnetic substances becomes paramagnetic when the temperature is increased above the "Curie Point," which may be defined as the steepest portion or point of inflection of the thermomagnetic curve. Although many properties of ferromagnetic substances are functions of the method of preparation, impurities, and previous magnetic history, the Curie Points usually are constant.

For magnetic analysis of ferromagnetic materials, modifications of the Fereday balance as described by Buehl and Wulff [29] and modifications of the Mathieu balance as described by Pichler and Merkel [30] have been used. The force on a sample placed in an inhomogeneous magnetic field is measured, the force exerted being related to the specific magnetization by equation 2. Since the magnetic moment is a function of field strength as well as temperature, it is necessary to compare magnetic moments at the same temperature and at equal field intensity or high intensity where the magnetic moment has reached its saturation value.

Qualitative analysis of ferromagnetic catalysts is based upon identification of Curie Points. The stability of ferromagnetic phases is important in the interpretation of thermomagnetic curves. For example, the Fe_2C carbides decompose to an appreciable extent at the temperatures given below.

$$Fe_2C\ (\text{hexagonal}) \xrightarrow{355°C} Fe_2C\ (\text{Hägg}) \xrightarrow{510°C} Fe_3C + C \qquad (3)$$

At higher temperatures oxides of iron may react with free carbon or carbides to form metallic iron. Quantitative analysis is possible from thermomagnetic curves. Although there are some uncertainties, the magnetic method of analysis of iron catalysts is usually more accurate than quantitative estimation of phases from x-ray diffraction patterns or chemical analysis. If two or more magnetic phases are present, the magnetic moment may be expressed as $M = \sum_i m_i \sigma_i$. For quantitative

[27] H. Konig, *Naturwiss.*, **33**, 71 (1946).
[28] R. Haul and T. Schoon, *Z. Elektrochem.*, **45**, 663 (1939).
[29] R. Buehl and J. Wulff, *Rev. Sci. Instruments*, **9**, 224 (1938).
[30] H. Pichler and H. Merkel, *U. S. Bur. Mines Tech. Paper* 718 (1949), 108 pp.

analysis the magnitude of the magnetic moment and its dependence upon temperature are determined on pure phases. The contribution of each phase is extrapolated from its Curie Point to a reference temperature, as shown in Figure 3 for a used iron catalyst containing chiefly magnetite and Fe_2C (Hägg).[31] This method, of course, can be used only

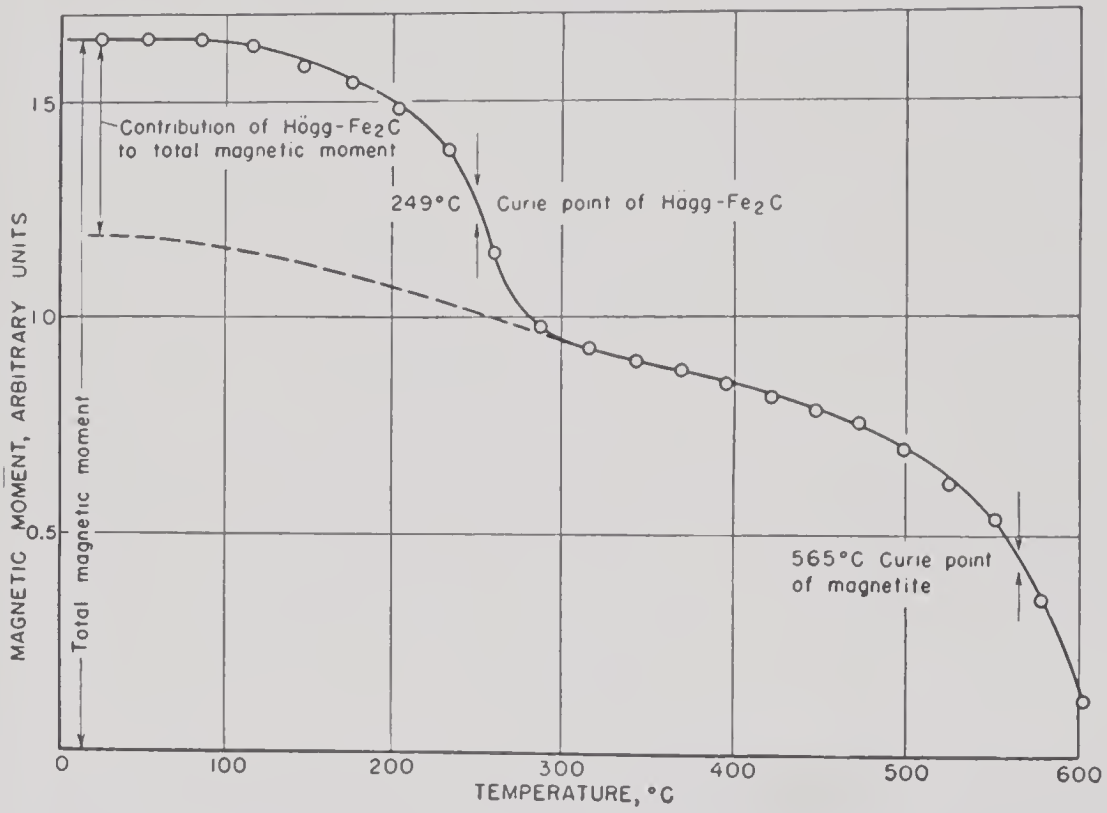


FIGURE 2–3. Thermomagnetic curve of a used iron Fischer-Tropsch catalyst containing Hägg Fe_2C and magnetite. The contribution of Hägg carbide to the total magnetic moment is estimated from the dotted extrapolation of the curve above 300°C to some lower reference temperature. Reproduced from reference 31.

in temperature ranges in which reactions of magnetic-phase decomposition or formation do not occur. If such reactions occur, interpretation of the data is more complicated and demands a thorough knowledge of the solid-phase reactions.

DENSITIES OF CATALYSTS

Three types of density are used in the study of catalysts:

Real density. This is determined by displacement of helium or an inert liquid and is the actual average density of the material comprising

[31] L. J. E. Hofer and E. M. Cohn, *Anal. Chem.*, **22**, 907 (1950).

the catalyst. Usually helium density is preferred because the small diameter of the helium atom permits it to penetrate very small pores and because the sample is not contaminated and can be used in subsequent experiments. In catalysts with only a few components these real densities can be used to check composition of catalysts as determined by chemical analysis and x-ray diffraction, the average density $\bar{\rho}$ being computed by $\bar{\rho} = \Sigma f_i \rho_i$, where f_i and ρ_i are the volume fraction and density of component i.

Bulk density. This is determined by measuring the weight of catalyst that can be packed into a unit volume. Bulk densities are somewhat arbitrary, depending upon the size of the vessel used and the method of packing into the vessel. For comparative data the same vessel (usually a graduate cylinder) is used, and the samples are tapped an equal number of times to produce a similar degree of packing. From bulk densities the weight of catalyst that will pack into a reactor can be computed.

Mercury density. Mercury will not wet most catalytic substances, and a pressure, p, is required to force the mercury into capillaries with openings of radius, r, against the surface tension of mercury, σ, as given by the capillary depression equation for cylindrical pores:

$$r = \frac{2\sigma \cos \theta}{p} \tag{4}$$

where θ is the angle of wetting. Ritter and Drake [32] used 140° as the value for θ. At atmospheric pressure mercury will penetrate only pores with openings larger than 5 microns. Determination of mercury densities at atmospheric pressure is simple and provides useful data regarding the pore structure. More elaborate experiments [32] in which mercury densities are determined at pressures up to 10,000 psi provide a distribution curve for pores with openings as small as 107 Å in diameter.

The pore volume is defined as the difference of the reciprocals of the mercury and helium densities, and it represents the volume of pores not penetrated by mercury, *ie*, pores with openings smaller than those predicted by equation 4. The difference of the reciprocals of the bulk and mercury densities is the volume of pores penetrated by mercury plus the void space between the catalyst particles. Data on mercury and helium densities of cobalt Fischer-Tropsch catalysts are discussed on pp. 66–71.

[32] H. L. Ritter and L. C. Drake, *Ind. Eng. Chem., Anal. Ed.*, **17**, 782, 787 (1945).

PHYSICAL ADSORPTION AS A METHOD OF ESTIMATING SURFACE AREA

Studies of the adsorption of gases and vapors on catalysts have yielded valuable information about catalytic processes, and in the next four sections adsorption experiments will be described. Adsorption processes may be divided into two types, physical adsorption and chemisorption. Physical adsorption involves van der Waals forces and is non-specific, occurring on all surfaces in a more or less similar manner. The amount of physical adsorption is very small above the critical temperature of the adsorbate. Below the critical temperature physical adsorption may be regarded as an "enhanced" condensation of the adsorbate, and layers several molecules in depth may form upon the surface. Usually, the heats of physical adsorption are less than twice the heat of liquefaction of the adsorbate. Physical adsorption is usually rapid and reversible. On the other hand, chemisorption involves high heats of adsorption of the order of magnitude of the formation of chemical bonds. Chemisorption is specific and forms no more than a monolayer on the surface. The rates of chemisorption vary from very rapid, so that the process appears to be instantaneous, to very slow. Slow chemisorption has been termed "activated adsorption" by Taylor.[33] In most cases chemisorption is irreversible.

Since catalytic reactions occur at surfaces, the determination of the extent and accessibility of the surface is important. If the chemical nature and the accessibility of the catalyst surface are the same for a series of catalysts, the activity should be directly proportional to the surface area. Most methods of estimating surface area by adsorption of gases involve, first, a way of determining the number of gas molecules corresponding to a monolayer and, second, an estimate of the cross-sectional area of the adsorbed molecules.

Determination of surface areas from chemisorption data is of uncertain accuracy, because it is difficult to estimate the volume of gas corresponding to a monolayer (even though equations such as Langmuir's[34] contain this term). Also, the estimation of a cross-sectional area for chemisorbed molecules is equally uncertain. Chemisorptions are specific and provide at best only the surface area of the chemisorbing component of the catalyst.

Physical adsorption at about the boiling point of the adsorbate is nonspecific; because the heats of adsorption are low, the cross-sectional area

[33] H. S. Taylor, *J. Am. Chem. Soc.*, **53**, 578 (1931); H. S. Taylor in *Eleventh Report of the Committee on Contact Catalysis*, John Wiley & Sons, New York, 1935, p 52.
[34] I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1,361 (1918).

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of the adsorbate molecules may be expected to be about the same as in the liquid or solid states. Emmett and Brunauer [35] and Brunauer, Emmett, and Teller [36] developed two methods of estimating from physical adsorption isotherms the number of molecules corresponding to a monolayer. In the first, the "point *B*" method, the volume of the monolayer corresponds to the start of the linear portion of the isotherm as shown in Figure 4. In the second method the volume of the mono-

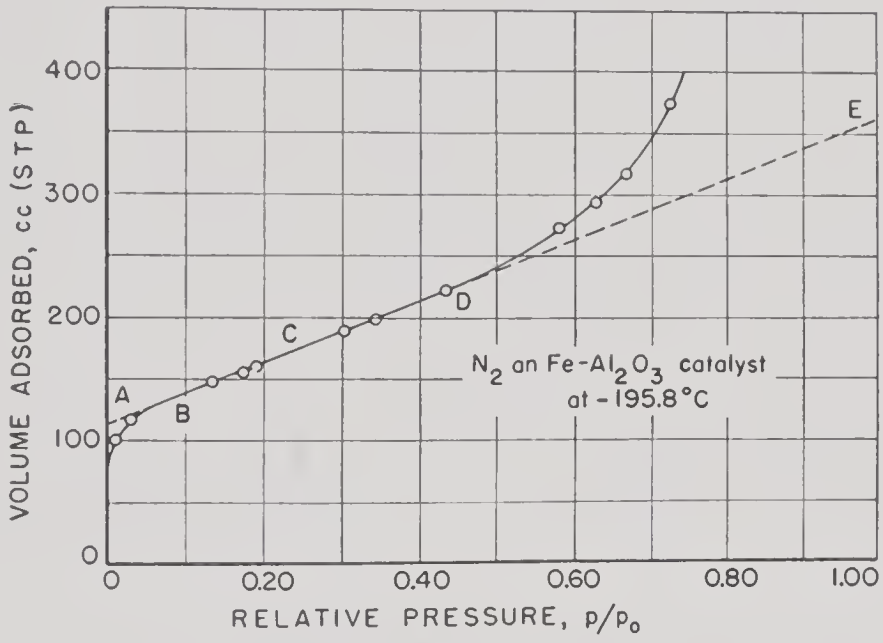


FIGURE 2–4. Adsorption isotherm, showing several possible points on the isotherm or extrapolations which were considered as representing the volume corresponding to a monolayer. Reproduced by permission from reference 36.

layer, V_m, is determined from the simple Brunauer, Emmett, and Teller (BET) equation. This equation is derived by equating the rate of adsorption to form an adsorbed layer to the rate of desorption from that layer. The heat of adsorption in the second and subsequent layers is assumed to be equal to the heat of liquefaction of adsorbate E_L; the heat of adsorption in the first layer E_1 is usually not equal to E_L. The simple BET equation is

$$\frac{V}{V_m} = \frac{cx}{(1 - x)[1 + (c - 1)x]} \tag{5}$$

where x is the relative pressure defined as $x = p/p_0$, p is the pressure at which a volume V (STP) of gas is adsorbed, and p_0 is the condensation

[35] P. H. Emmett and S. Brunauer, *ibid.*, **57**, 1,754 (1935); **59**, 1,553, 2,682 (1937).

[36] S. Brunauer, P. H. Emmett, and E. Teller, *ibid.*, **60**, 309 (1938).

pressure (vapor pressure) of the adsorbate at the temperature of the adsorption, and

$$c = \frac{a_1 b_2}{a_2 b_1} e^{(E_1 - E_L)/RT} \tag{6}$$

where the ratio of the adsorption and desorption rate constants for the first and second layers, $a_1 b_2 / a_2 b_1$, is usually assumed equal to 1. The equation may be rearranged into the linear form

$$\frac{x}{V(1-x)} = \frac{1}{V_m c} + \frac{c}{V_m (c-1)} x \tag{7}$$

for evaluation of constants V_m and c. Equation 5 gives the proper shape of adsorption isotherms on non-porous solids; however, this equation fits the data exactly only over the range of relative pressure of 0.05–0.35, as shown in Figure 5. Nevertheless, the equation is satisfactory for the estimation of V_m from all types of physical adsorption isotherms except those characteristic of charcoals (type I of Brunauer's classification; see p 56). In most cases except for isotherms with values of c less than 5, V_m is very nearly equal to the value estimated by the "point B" method.

Usually the cross-sectional area of the adsorbate is estimated from the liquid density by the method of Emmett and Brunauer.[35] However, accumulated evidence shows that this method does not give identical surface areas for adsorption of different molecules on the same adsorbent, and some corrections in the method of estimating the cross-sectional area of molecules are probable necessary.[37] However, as shown below, the value assigned to the nitrogen molecule probably is satisfactory.

An equation derived by Harkins and Jura,[38] based on a type of spreading force-area relationship observed for insoluble films on liquids, gives surface areas in general agreement with the BET method. A plot of the Harkins-Jura equation

$$\log x = \frac{A}{V_2} + B \tag{8}$$

where A and B are constants, gives straight lines over wide ranges of relative pressures. The surface area is related to constant A by the equation

$$\text{surface area} = kA^{1/2} \tag{9}$$

where k is a constant which must be determined by some independent

[37] R. A. Beebe, J. B. Beckwith, and J. M. Honig, *ibid.*, **67**, 1,554 (1945).
[38] W. D. Harkins and G. Jura, *ibid.*, **66**, 1,366 (1944).

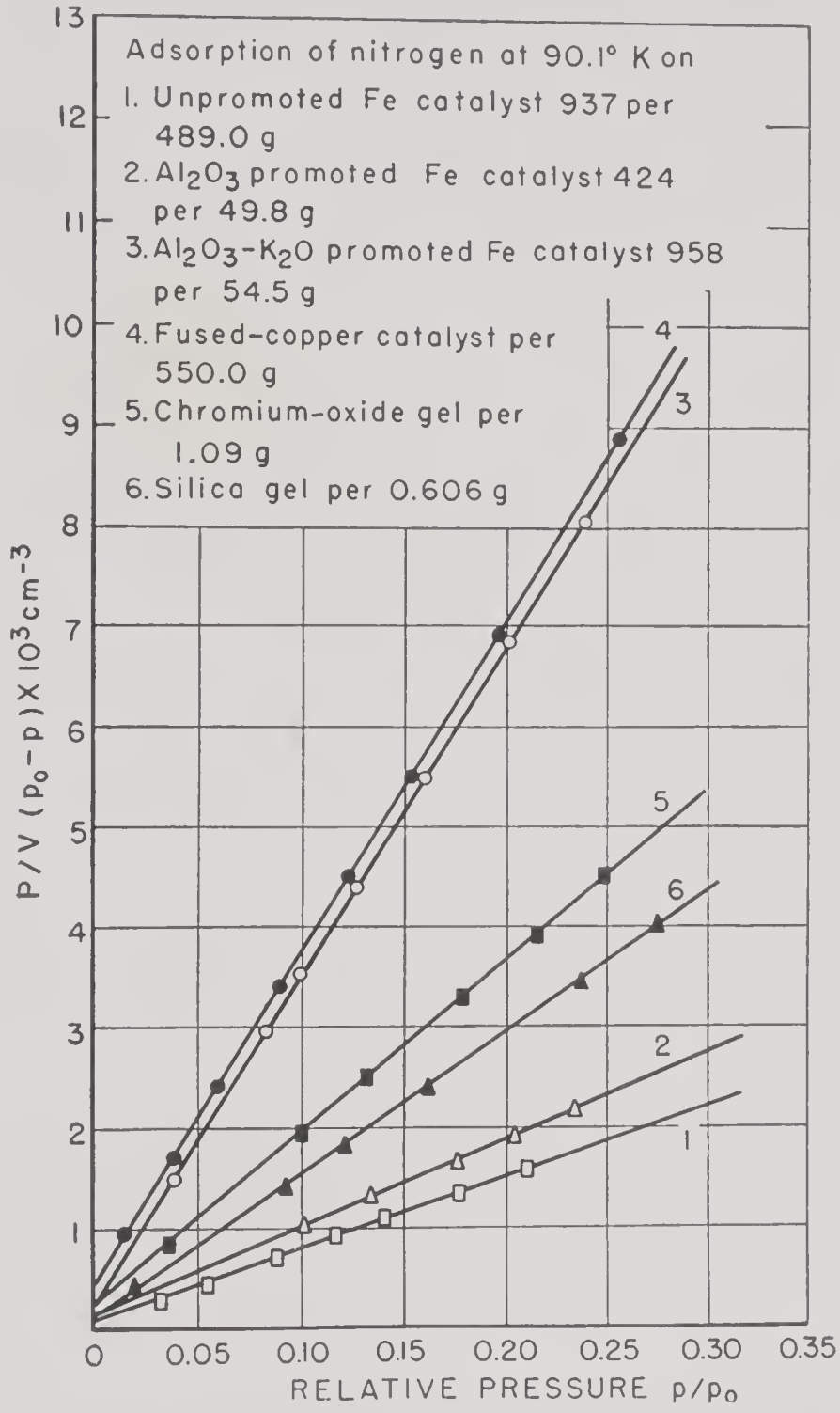


FIGURE 2–5. Linear plots of the Brunauer, Emmett, and Teller equation (equation 7) for nitrogen adsorption isotherms of various adsorbents. Reproduced by permission from reference 36.

method. Emmett [39] has discussed the relationship of this method to the BET method. Emmett [40] and Brunauer [41] have estimated that the surface area determined by the BET method has an absolute uncertainty of less than 20 per cent. Comparison of these surface areas with those estimated from microscopic [40,42] and electron microscopic particle [43] size distribution substantiates this estimate. Excellent agreement was also obtained between the BET areas and those of the "absolute method" of Harkins and Jura.[44] In the "absolute method" a non-porous powder on which four or more molecular layers of vapor of a liquid are adsorbed is immersed in a large quantity of that liquid in a sensitive calorimeter. The heat evolved is equated to the product of surface area times surface enthalpy of the adsorbed liquid. In the fourth and subsequent layers the surface enthalpy is equal to the surface enthalpy of the normal liquid, $\gamma + T\frac{d\gamma}{dT}$, where γ is the normal surface tension of the liquid. By this method, areas of two samples of TiO_2 were found to be 13.8 and 8.9 sq m per g, as compared with 13.8 and 9.6 sq m per g by the BET method.

ESTIMATION OF PORE SIZE DISTRIBUTION FROM PHYSICAL ADSORPTION ISOTHERMS

Brunauer, Deming, Deming, and Teller [41,45] proposed five general types of isotherms (Figure 6) which can be explained on the bases of c values and pore structures. Rough estimates of the ranges of pore sizes corresponding to the different isotherm types are as follows: type I, less than 25 Å in diameter; types IV and V, 25 to 200 Å; and types II and III, greater than 200 Å. Types II and IV correspond to systems for which the value of c is greater than 1, and types III and V to those with c values equal to or less than 1. By comparison of a given isotherm with those of Figure 6, a qualitative estimate of the pore distribution may be made. Some isotherms appear to be composites of two or more of these types.

Numerous variations of the BET equation have been developed for adsorption on porous adsorbents. Brunauer, Emmett, and Teller,[36]

[39] P. H. Emmett, *ibid.*, **68**, 1,784 (1946).

[40] P. H. Emmett, in Kraemer's *Advances in Colloid Science*, Interscience Press, New York, 1942.

[41] S. Brunauer, *Physical Adsorption*, Princeton University Press, Princeton, N. J., 1943.

[42] H. M. Barrett, A. W. Birnie, and M. Cohen, *J. Am. Chem. Soc.*, **62**, 2,839 (1940).

[43] R. B. Anderson and P. H. Emmett, *J. Applied Phys.*, **19**, 367 (1948).

[44] W. D. Harkins and G. Jura, *J. Am. Chem. Soc.*, **66**, 1,362 (1944).

[45] S. Brunauer, L. S. Deming, W. E. Deming, and E. Teller, *ibid.*, **62**, 1,723 (1940).

Brunauer, Deming, Deming, and Teller,[45] and Pickett [46] have derived equations for adsorption in "condenser plate" pore systems. Anderson and Hall [47] proposed an equation for porous adsorbents in which the area of each subsequent layer is less than the one underlying it. Although the range over which the equations satisfactorily fit the experimental data is extended to higher relative pressures, these equations do

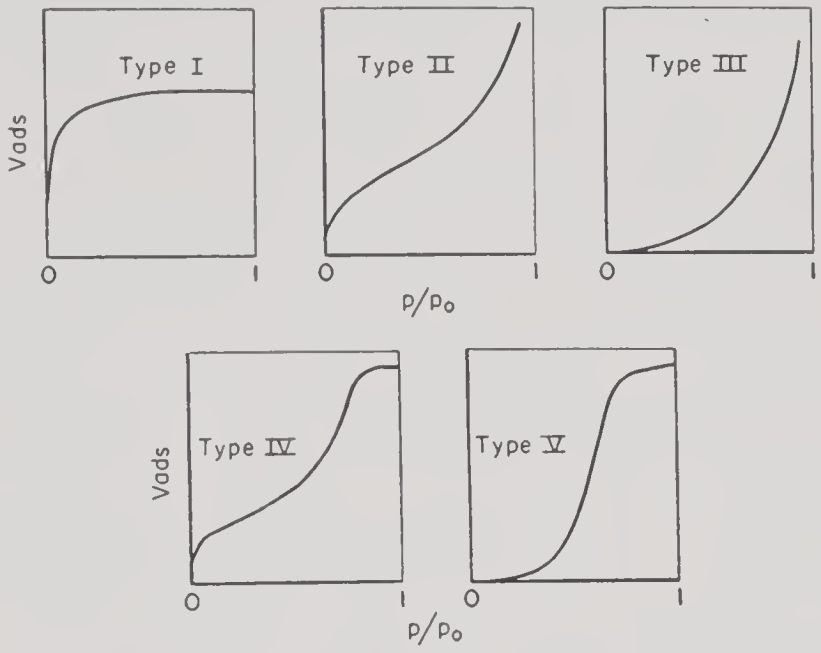


FIGURE 2–6. Five types of van der Waals adsorption isotherms. Reproduced by permission from reference 45.

not, in general, contribute much more information than the simpler methods described below.

If the pore volume of the adsorbent can be determined, an average pore diameter, d, may be estimated from equation 10, proposed by Emmett and DeWitt [48] for cylindrical pores,

$$d = \frac{4V}{S} \tag{10}$$

where V is pore volume and S the surface area. The significance of this method has been discussed by Anderson and Hall.[47] For types I, IV, and V, the pore volume may be estimated by the volume of adsorbate computed as normal liquid corresponding to the flat portion of the isotherm at high relative pressures. For adsorbents that give isotherms of types II and III, the pore volume cannot be determined from the iso-

[46] G. Pickett, *ibid.*, **67**, 1,958 (1945).
[47] R. B. Anderson and W. K. Hall, *ibid.*, **70**, 1,727 (1948).
[48] P. H. Emmett and T. W. DeWitt, *ibid.*, **65**, 1,253 (1943).

therms, but may be estimated from the differences of the reciprocals of mercury and helium densities. However, unless mercury densities are determined at high pressures the pore volume may be very much larger than that containing the pores contributing most of the surface areas, and the average pore diameters computed by equation 10 must be regarded as an upper limit of the average pore diameter.

Pore diameters may also be estimated from the Kelvin equation applied to the desorption branch of the isotherm,

$$\ln x = \frac{2\sigma V \cos\theta}{rRT} \tag{11}$$

where x is the relative pressure at which desorption occurs from a cylindrical pore of radius r, σ and V are the surface tension and molar volume of the normal liquid, respectively, and θ is the angle of wetting (usually assumed to be zero). Since the surface of a capillary after desorption has occurred is covered with the number of layers normally expected for multilayer adsorption at that pressure, the radius r is usually 1–2 molecular diameters smaller than the actual pore radius. Usually for types IV and V isotherms the average pore radius is estimated from the relative pressure corresponding to the steepest part of the desorption isotherm. Shull [49] has proposed a method of approximating the pore size distribution from the desorption isotherms. In many cases average pore diameters estimated from the Kelvin equation for type IV isotherms agree closely with those from equation 10.[48]

CHEMISORPTION STUDIES

In most catalytic processes it may be expected that at least one of the reactants should be chemisorbed on the catalyst; however, the relationship between catalytic activity and chemisorption is not simple. For example, if molecules of reactants, products, or other components are too firmly adsorbed, they may not enter into the catalytic reaction, but will act as a poison by blocking off that portion of the surface.

Adsorption isobars have yielded some of the more interesting information about chemisorption processes. These data indicate that at least two types of activated adsorption can occur on the same catalyst, and it appears that the different types of adsorption occur on different parts of the surface. Isobars of hydrogen on an iron synthetic-ammonia catalyst, on nickel, and on zinc oxide are presented in Figures 7, 8, and

[49] C. G. Shull, *ibid.*, **70**, 1,405 (1948); C. G. Shull, P. B. Elkin, and L. C. Roess, *ibid.*, **70**, 1,410 (1948).

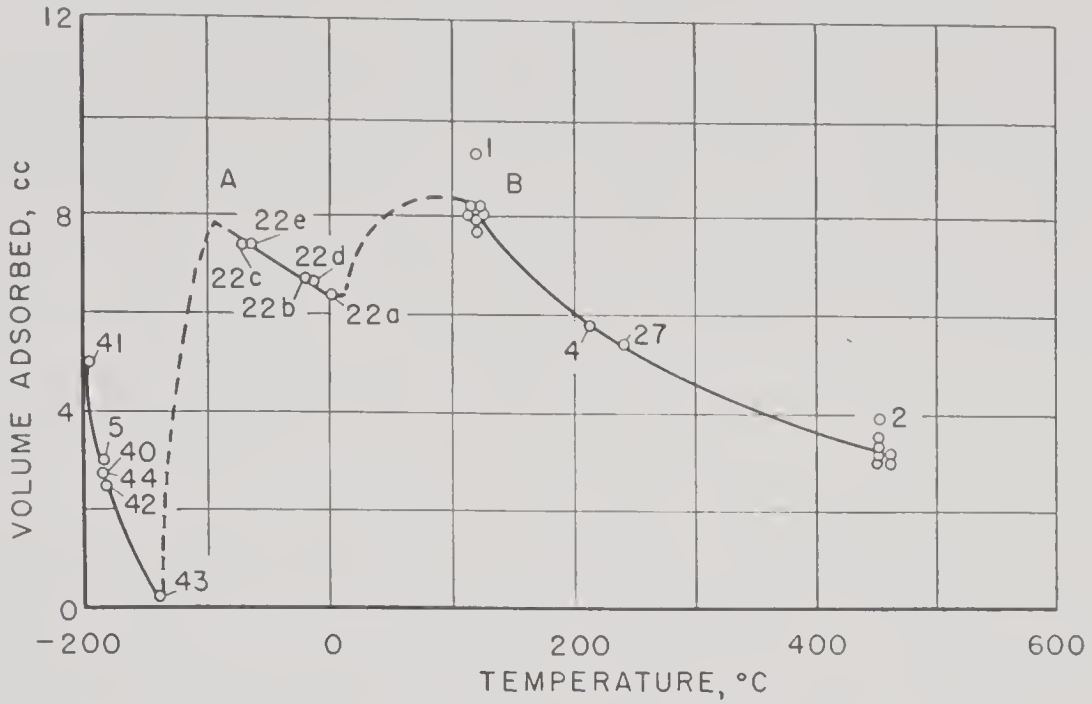


FIGURE 2–7. Adsorption isobar of hydrogen on an iron synthetic-ammonia catalyst with pressure of hydrogen of 760 mm Hg, showing maxima corresponding to types *A* and *B* chemisorptions. Reproduced by permission from reference 50.

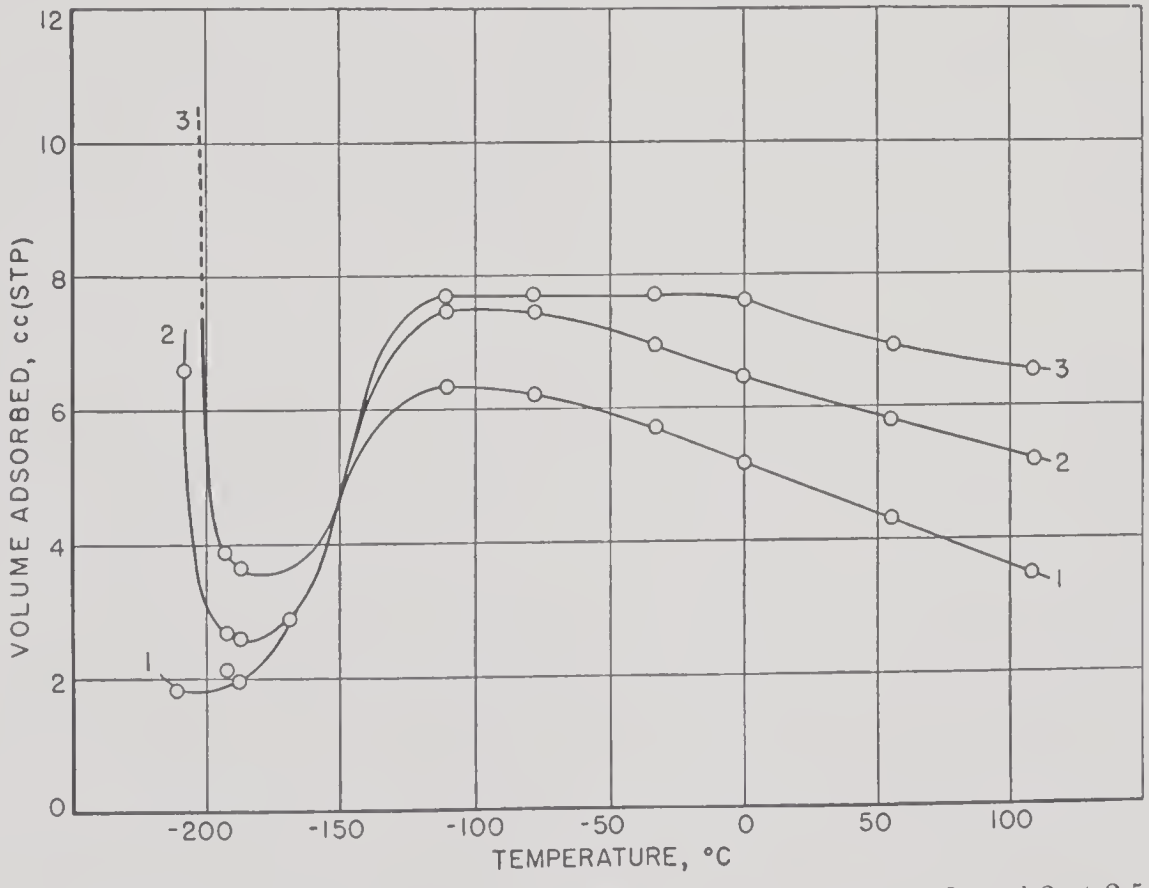


FIGURE 2–8. Adsorption isobars of hydrogen on nickel. Curves 1, 2, and 3 at 2.5, 20, and 60 cm Hg pressure, respectively. Reproduced by permission from reference 51.

9, respectively. The volume adsorbed on the iron catalyst (Figure 7) decreased as the temperature was raised to about −100°C, then increased to point *A* and again decreased; above 0°C it increased to point *B* and finally decreased.[50] At points *A* and *B* the rates of adsorption

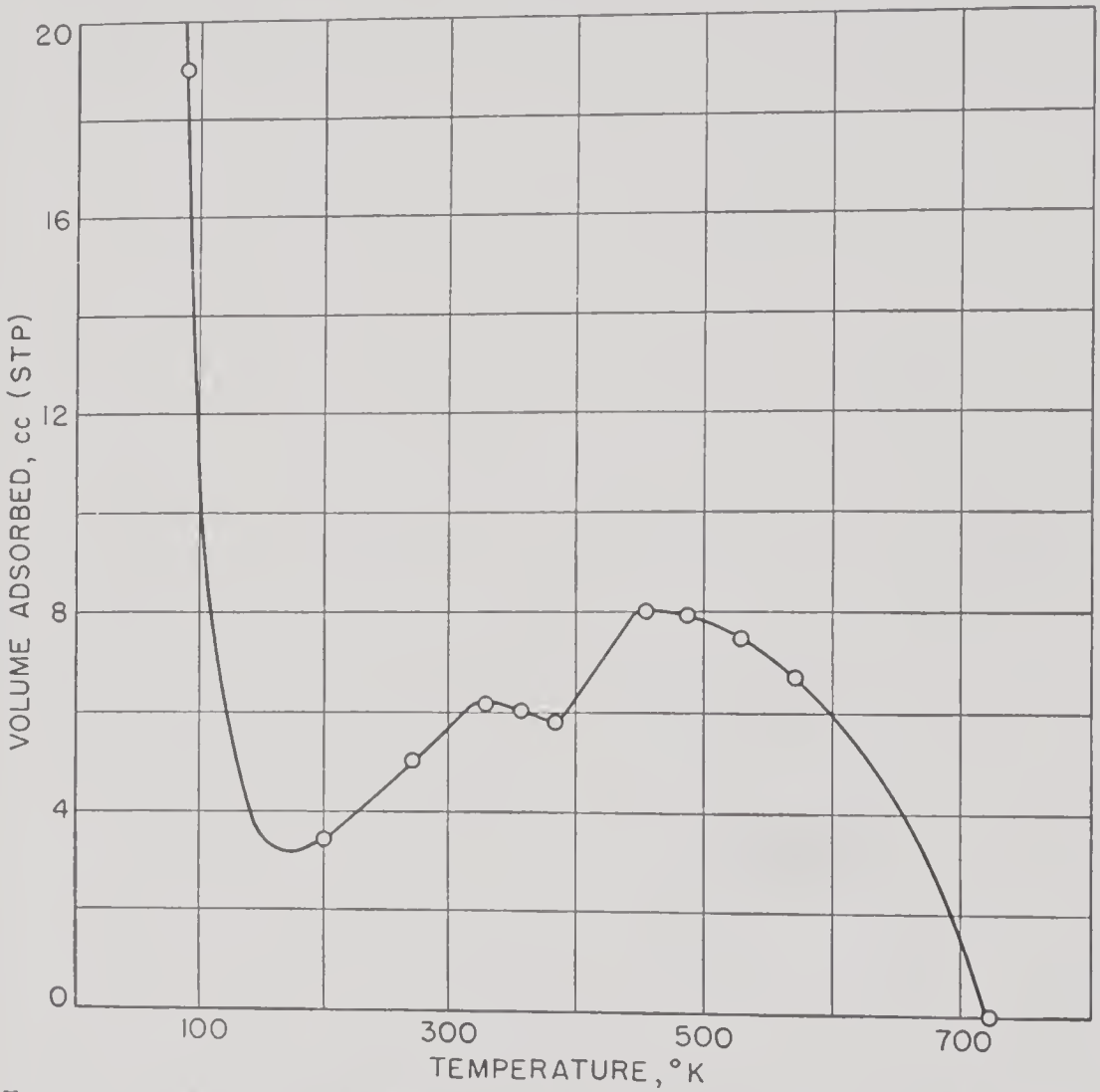


FIGURE 2-9. Adsorption isobar of hydrogen on zinc oxide at 760 mm Hg pressure. Reproduced by permission from reference 52.

were quite slow, and the rates of both types *A* and *B* chemisorption increased with temperature. The isobars of hydrogen on nickel (Figure 8) show a minimum at −200° to −150°C and a broad maximum from −100° to 0°C.[51] The hydrogen isobar on zinc oxide (Figure 9) shows maxima at 25° and 200°C.[52]

Taylor's theory of activated adsorption [33] explains this phenomenon.

[50] P. H. Emmett and R. W. Harkness, *ibid.*, **57**, 1,631 (1935).
[51] A. F. Benton and T. A. White, *ibid.*, **52**, 2,325 (1930).
[52] H. S. Taylor and C. O. Strother, *ibid.*, **56**, 586 (1934).

For example, on iron, three types of adsorption of hydrogen occur (probably on different adsorption sites), that below $-100°C$ probably being a mixture of physical and chemisorption and types A and B being activated adsorptions. The activated adsorptions have high energies of activation so that at low temperatures their rates are essentially zero, and true equilibrium is not attained. Thus, at $-100°C$ the low-temperature adsorption was virtually zero, and types A and B activated

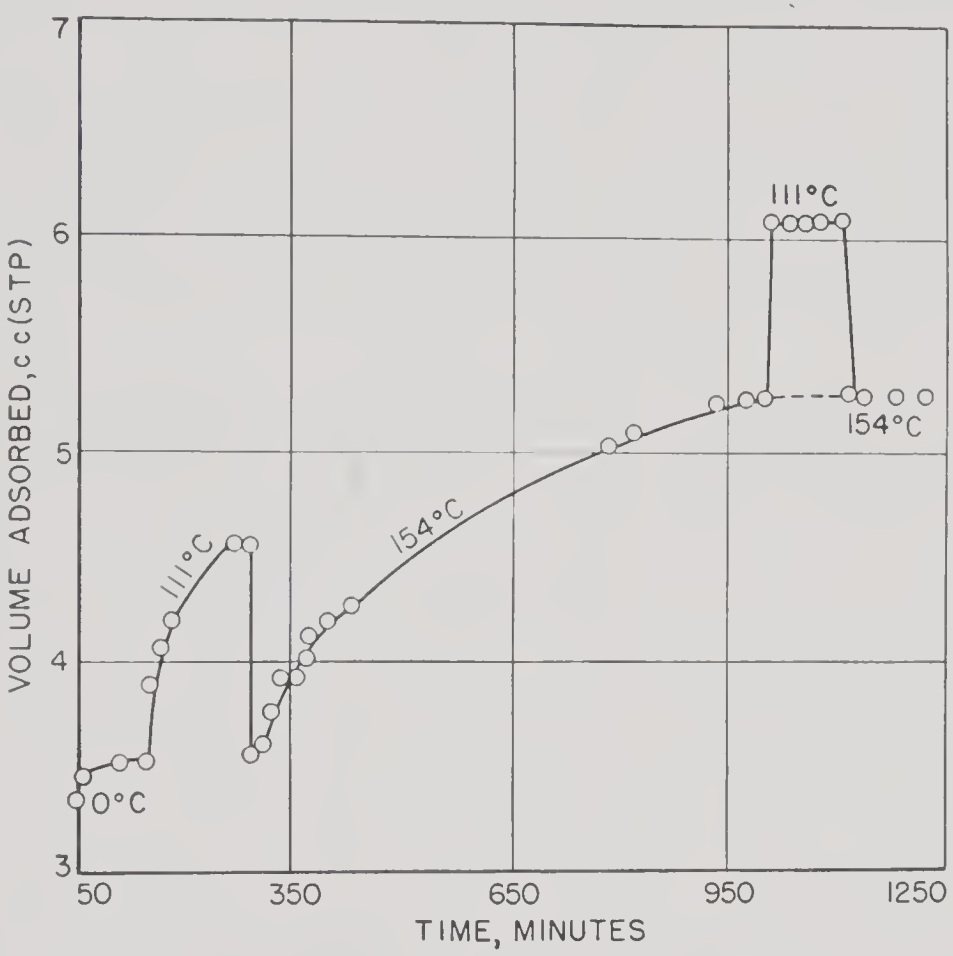


FIGURE 2–10. Volume of hydrogen adsorbed on zinc oxide as functions of time and temperature. Reproduced by permission from reference 53.

adsorption did not occur at appreciable rates. At $-78°C$ type A chemisorption occurred at an appreciable rate, and above 100°C the rate of type B adsorption became appreciable.

The maxima in the isobars (Figures 7, 8, and 9) are observed on increasing the temperature. If the temperature is decreased the isobar is not retraced, *ie*, the activatedly adsorbed molecules are thermodynamically stable and do not desorb. Taylor and Liang [53, 54] studied isobars and rates of adsorption of hydrogen on zinc oxide and other oxide cata-

[53] H. S. Taylor and S. C. Liang, *ibid.*, **69**, 1,306, 2,989 (1947).

[54] H. S. Taylor, in *Advances in Catalysis*, Academic Press, New York, 1948.

lysts at both increasing and decreasing temperatures. A typical plot of volume of hydrogen adsorbed on zinc oxide as a function of time is shown in Figure 10. When the temperature was first increased from 111°C to 154°C the volume of hydrogen decreased almost instantaneously and then slowly increased until the total volume adsorbed at about 1,000 min was considerably greater than at 111°C. When the temperature was lowered again to 111°C the volume adsorbed increased rapidly, the in-

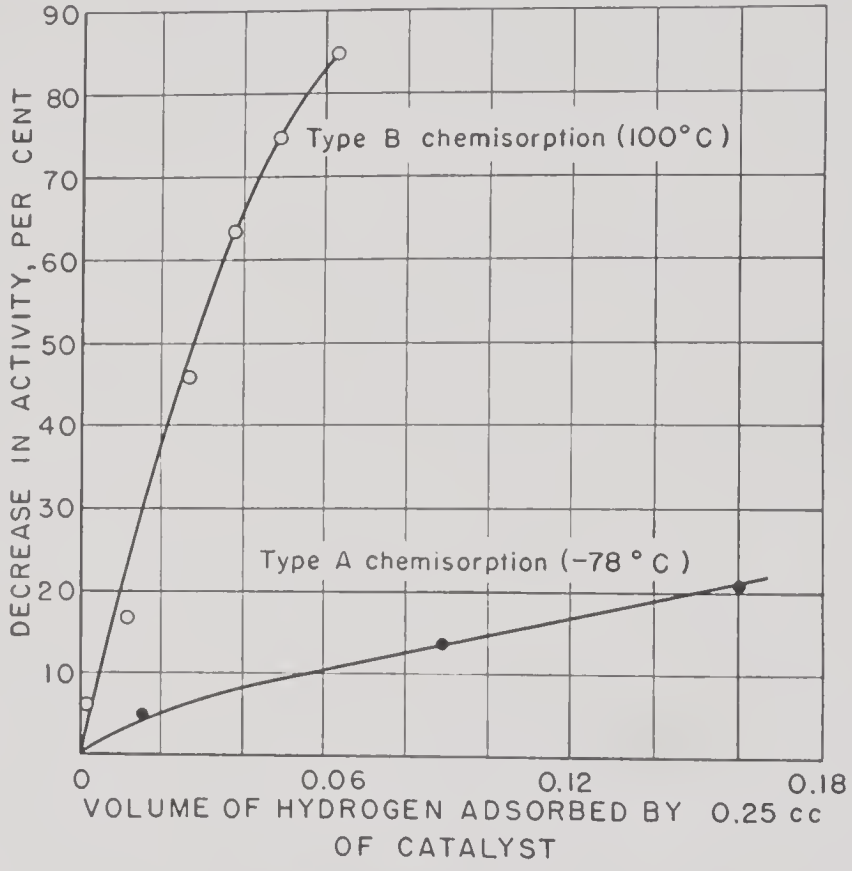


FIGURE 2–11. Poisoning effect of activated adsorption of hydrogen on the rate of *ortho-* to *para*-hydrogen conversion at −190°C on catalyst 931. Reproduced by permission from reference 55.

crease being equal to the immediate decrease observed when the temperature was raised. On increasing the temperature to 154°C again, the volume adsorbed decreased by this amount. These data are strong evidence for the concept of heterogeneity of catalyst surfaces; *ie*, the different types of adsorption occur on different portions of the surface.

Heterogeneity of surface of iron catalysts was demonstrated by the experiments of Emmett and Harkness [55] with the catalytic interconversion of *ortho-* to *para*-hydrogen. The rate of conversion was determined at −190°C on a thoroughly reduced catalyst after evacuation at

[55] P. H. Emmett and R. W. Harkness, *J. Am. Chem. Soc.*, **57**, 1,624 (1935).

500°C followed by: (*a*) cooling below −100°C before exposing sample to hydrogen; (*b*) chemisorption of hydrogen at −78°C (type *A*), and (*c*) chemisorption of hydrogen at +100°C (type *B*). The retardation of the rate by types *A* and *B* chemisorbed hydrogen is shown in Figure 11. Types *A* and *B* chemisorbed hydrogen retard the reaction to different extents, type *B* being more effective than type *A*. Thus, the two chemisorptions probably occupy different portions of the surface. The fact that type *B* adsorption is most effective indicates that it is primarily a chemisorption and not solution of hydrogen in iron. Systems exhibiting more than one type of chemisorption are not limited to those involving hydrogen [see article of Hunsmann [55a] for numerous examples of chemisorption].

ADSORPTION AND PORE VOLUME STUDIES OF CATALYSTS

In this section adsorption data on iron synthetic-ammonia catalysts and adsorption and pore volume data on cobalt and nickel Fischer-Tropsch catalysts will be discussed.

Iron Synthetic-Ammonia Catalysts

Brunauer and Emmett [1, 56] have made an extensive study of the adsorption of gases on iron synthetic-ammonia catalysts. The adsorption isobar of hydrogen on these catalysts has been discussed previously (p 58), and the chemisorption of nitrogen will be discussed in a later section because of its implications in the mechanism of the ammonia synthesis (p 91). Brunauer and Emmett studied the adsorption of nitrogen and a number of other simple molecules such as argon, methane, oxygen, carbon monoxide, carbon dioxide, and *n*-butane on reduced promoted and unpromoted synthetic-ammonia catalysts at temperatures near the respective boiling points of the gases. Oxygen, carbon monoxide, and carbon dioxide isotherms were a composite of physical and chemisorption. It was possible to remove only the physically adsorbed gas by pumping the sample at a temperature about 100°C higher than the temperature of adsorption, and then a second isotherm gave a good approximation of the physical isotherm. These isotherms were used in selecting the "point *B*" method of estimating the volume of the monolayer.

[55a] W. Hunsmann in G. M. Schwab, *Handbuch der Katalyse*. IV. *Heterogene Katalyse* I, Springer-Verlog, Vienna, 1943 (reprinted by Edward Brothers, Inc., Ann Arbor, 1945), pp 405–72.

[56] P. H. Emmett and S. Brunauer, *ibid.*, **59**, 310, 1,553 (1937).

Table 2 presents the surface areas of the series of synthetic-ammonia catalysts as estimated from nitrogen isotherms by the "point *B*" method as well as the activities of some of these catalysts in the ammonia syn-

TABLE 2. SURFACE AREA AND ACTIVITIES OF IRON SYNTHETIC-AMMONIA CATALYSTS

Catalyst	Promoters		Conditions of Reduction and Sintering	Surface Area,[a] sq m per g	Activity, per cent NH_3[b]
	Name	Quantity, per cent			
973 I	Al_2O_3	0.15	124 hr at 300°–350°C plus 54 hr at 375°–500°C	0.38	3.3
973 II	Al_2O_3	0.15	96 hr at 300°–400°C	0.94	
954 I	Al_2O_3	10.2	48 hr at 350°–450°C plus 48 hr at 450°–500°C	8.38	8.2
931 I	Al_2O_3 K_2O	1.30 1.59	18 hr at 300°–350°C, 65 hr at 350°–450°C, and 18 hr at 450°–530°C	3.33	12.3
931 II	Al_2O_3 K_2O	1.30 1.59	18 hr at 300°–350°C, 65 hr at 350°–450°C, and 18 hr at 450°–530°C, plus sintering at 475°C	3.01	
931 III	Al_2O_3 K_2O	1.30 1.59	18 hr at 300°–350°C, 65 hr at 350°–450°C, and 18 hr at 450°–530°C, plus several partial oxidations and reductions at 450°C	2.46	
958	Al_2O_3 K_2O	0.35 0.08	36 hr at 350°–450°C plus 36 hr at 450°–500°C	1.90	10.4
930	K_2O	1.07	48 hr at 350°–450°C	0.43	5.3
424	Al_2O_3 ZrO_2	1.03 0.19	Conditions not specified	7.12	

[a] Surface areas per gram of unreduced catalyst as estimated by the "point *B*" method.

[b] Activity expressed at per cent ammonia formed at 450°C, 100 atm, and a space velocity of 5,000. Equilibrium percentage of ammonia under these conditions is 16.4 per cent.

thesis. The unreduced catalysts had very low surface areas, almost all of the area of the reduced catalysts being developed in the reduction. The most interesting feature of the table is the effect of the promoters in the development of the surface area of the reduced catalysts. Nearly pure iron catalyst 973 had a low surface area when reduced at 400°C; on sintering at 500°C the area dropped to less than half of its previous value. Catalyst 930 promoted with potassium oxide had an area as low as the pure iron catalyst. Catalysts 954 promoted with alumina and 424 promoted with alumina and zirconia had surface areas at least ten times greater than 973 and 930. Catalysts 931 and 958 promoted with alumina and potassium oxide also had areas considerably greater than 973 and 930. Thus alumina and zirconia in these catalysts are structural promoters; one of the functions of structural promoters is the formation and maintenance of a high-area structure on reduction. The structural promotion by alumina was also shown by the x-ray diffraction studies of Wyckoff and Crittenden [9] (p 42). The data indicate that potassium oxide is not a structural promoter. However, the activity data indicate that the catalysts containing potassium oxide are more active per unit surface area.

In a later paper, Brunauer and Emmett [57] studied the chemisorption of nitrogen, carbon monoxide, carbon dioxide, and hydrogen on these catalysts and related the amount of chemisorbed gas to the physical nitrogen monolayer, these data being summarized in Table 3. The authors believed the chemisorptions of carbon monoxide and carbon dioxide to be molecular and those of hydrogen and nitrogen to be atomic. The physical adsorption of nitrogen gives an estimate of the total surface area. The low-temperature (−183°C) chemisorption of carbon monoxide is an indication of the fraction of surface occupied by iron atoms. With nearly pure iron catalyst 973 the ratio of chemisorbed carbon monoxide to the physical nitrogen monolayer was 1.13; this ratio is not unreasonable since a layer of chemisorbed molecules may be more densely packed than a physically held layer. The presence of promoters decreased this ratio, potassium oxide being the most effective. Carbon dioxide was chemisorbed on the potassium oxide at the surface of the catalysts. If the carbon dioxide is adsorbed in a monolayer on only the potassium oxide surface, an estimate may be made of the fraction of the surface occupied by each component of the catalyst. Thus, in the alkali-free catalysts 954 and 424, the oxide promoters probably cover about 55 and 35 per cent of the surface, respectively. About 70 per cent of the surface of catalyst 930 is covered by the 1.07 per cent potassium oxide. In catalyst 958 about 62 per cent of the surface consisted of iron atoms,

[57] S. Brunauer and P. H. Emmett, *ibid.*, **62**, 1,732 (1940).

TABLE 3. CHEMISORPTION ON IRON SYNTHETIC-AMMONIA CATALYSTS

Catalyst	Promoters		CO Chemi [a] / N_2 Monolayer	CO_2 Chemi [b] / N_2 Monolayer	H_2 Chemi [c] / CO Chemi		N_2 Chemi [d] / CO Chemi	N_2 Chemi [d] / N_2 Monolayer
	Name	Quantity, per cent			Type *A*, −78°C	Type *B*, 100°C		
973	Al_2O_3	0.15	1.13	0.13	0.40	0.41	0.24	0.35
954	Al_2O_3	10.2	0.43	0.05	0.57	0.59	0.34	0.15
424	Al_2O_3	1.03	0.65	0.08				
	ZrO_2	0.19						
930	K_2O	1.07		0.74				
931	Al_2O_3	1.30	0.44	0.61	0.94	0.95	0.50	0.26
	K_2O	1.59						
958	Al_2O_3	0.35	0.62	0.27	0.50			
	K_2O	0.08						

[a] Carbon monoxide chemisorbed at −183°C.
[b] Carbon dioxide chemisorbed at −78°C.
[c] Time of equilibration 1 hr or longer.
[d] Nitrogen chemisorbed at 391°–395°C.

27 per cent potassium oxide, and the remaining 11 per cent alumina. In catalyst 931 there appears to be no free alumina on the surface, the alumina and potassium oxide presumably being combined on the surface. Thus, the promoters collect on the surface in greater quantities than in the bulk phase of the catalyst, this tendency being greater for potassium oxide than alumina. This conclusion agrees with the observation that alkali is readily volatilized from singly promoted catalysts and can be readily extracted with water from the raw singly and doubly promoted catalysts. Also, the order of addition of alkali, whether before or after the fusion, does not greatly change the activity of the resulting catalysts.[58] Thus, it appears that the potassium oxide is not completely incorporated into raw catalysts. The alumina is in solid solution with the magnetite, and its accumulation on the surface on reduction is to be expected because the reduced iron atoms occupy less volume than the iron oxide. It may be postulated that the iron atoms will recede from the reduction zone, leaving a matrix of alumina. This alumina on the surface prevents the iron atoms from migrating and forming structures of lower surface area.

Brunauer and Emmett [57] also studied the effect of the chemisorption of one gas upon the chemisorption of another, but these studies are too detailed for this discussion. From these data and those of Table 3, it was concluded that the surface was heterogeneous, probably because of differently developed crystal faces.

[58] J. F. Shultz, private communication.

Cobalt Fischer-Tropsch Catalysts

Anderson, Hall, Hewlett, Hofer, and Seligman [2,59] studied the properties of unreduced and reduced cobalt Fischer-Tropsch catalysts. In

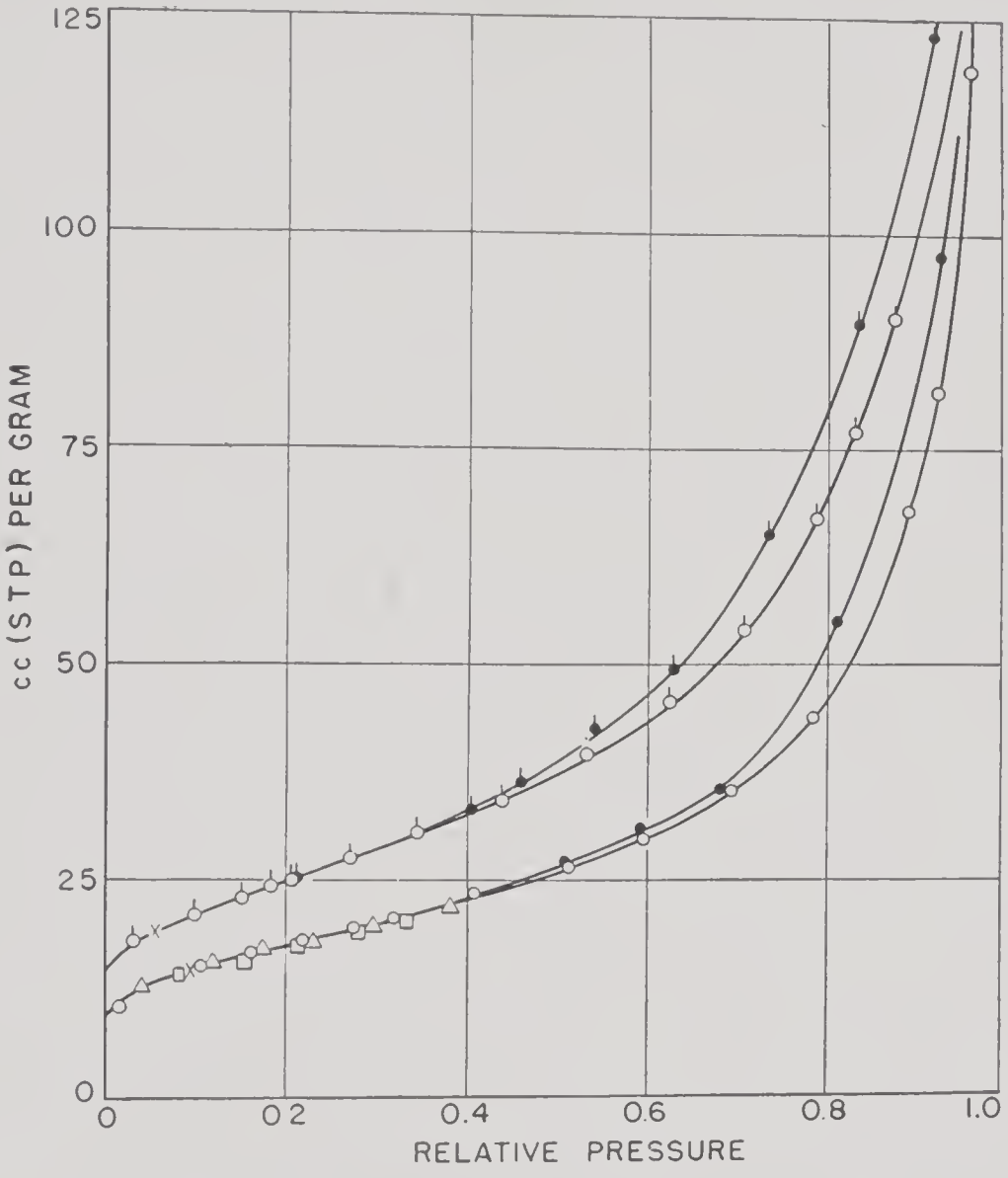


Figure 2–12. Adsorption of nitrogen at −195°C on unreduced and reduced cobalt catalyst 89J, where ♁ represents the unreduced catalyst and ○, □, and △ represent different samples of reduced catalyst. Desorption points are solid, and the volume of gas corresponding to a monolayer is represented by ×. Reproduced by permission from reference 59.

Figure 12 are shown nitrogen isotherms of raw and reduced Co-ThO_2-MgO-kieselguhr catalyst, 89J. The shape of the isotherms and the small amount of hysteresis indicate that the catalyst has a system of relatively

[59] R. B. Anderson, W. K. Hall, H. Hewlett, and B. Seligman, *J. Am. Chem. Soc.*, **69**, 3,114 (1947).

TABLE 4. SURFACE AREAS OF UNREDUCED AND REDUCED COBALT FISCHER-TROPSCH CATALYSTS

Catalyst	Form [a]	Kieselguhr [b]	Method of Reduction [c]			Surface Areas of Catalysts, sq m				Ratio of Area of Complex after:before Reduction
			Temperature, °C	Time, hr	Per Cent Weight Loss	Unreduced		Reduced		
						Total, per g	Complex, per g of complex	Total,[d] per g	Complex,[e] per g of complex	
Co:ThO_2:MgO:Kg = 100:6:12:200										
89H	P	H.S.C.	400	2	19.8	67.2	127.2	41.9	83.8	0.620
89J	P	F.C.	400	2	17.4	85.5	155.4	62.0	99.6	0.640
89K	P	Port.	400	2	19.7	88.8	160.3	62.7	105.5	0.651
89K	G	Port.	400	2	17.7	101.1	185.0	62.2	104.5	0.580
Co:ThO_2:MgO = 100:6:12	G	None	400	2	37.7	154.8	154.8	52.8	52.8	0.341
Co:ThO_2 = 100:6	G	None	400	2	38.7	171.0	171.0	14.6	14.6	0.085
Co:MgO [f] = 100:12	G	None	400	2	41.6	142.6	142.6	35.2	35.2	0.247
Co:MgO [g] = 100:8	G	None	400	2	42.0	129.6	129.6	18.3	18.3	0.141
Co:Kg = 100:200	G	F.C.	400	2	21.1	75.6	124.7	18.3	14.2	0.109
Co:Kg = 100:200	G	H.S.C.	400	2	21.2	77.2	152.4	6.87	12.0	0.078
Cobalt basic carbonate	G	None	400	2	44.2	126.2	126.2	2.5	2.5	0.020
Cobalt oxide powder	[h]	None	250	24	30.2	67.0	67.0	3.2	3.2	0.048

[a] G = granules, broken filter cake; P = pellets (1.6 mm long by 3.2 mm diameter).
[b] H.S.C. = Johns-Manville Hyflo Super-Cel; F.C. = Johns-Manville Filter-Cel; Port. = Portuguese kieselguhr.
[c] All reductions except cobalt oxide powder were made with hydrogen at space velocities per hour of 6,000. Cobalt oxide powder was reduced in hydrogen at a space velocity of 100.
[d] Per gram of unreduced catalyst.
[e] Per gram of complex in unreduced catalyst.
[f] Contains powdered magnesia.
[g] Contains precipitated magnesia.
[h] A fine powder.

large pores (greater than 200 Å). In Table 4 are presented surface areas of raw and reduced Co-ThO_2-MgO-kieselguhr catalysts and of similar preparations which lack one or more of these components. The area of the cobalt-promoter complex is computed, assuming that the area of the kieselguhr is additive (see footnote 7 of reference 2). The data of Table 4 indicate that the catalyst containing both promoters and carrier was the most resistant to sintering during reduction. Of the promoters, the mixture of thoria and magnesia was the most effective while magnesia alone was more effective than thoria. The kieselguhr was about as effective as the thoria in preventing sintering.

Cobalt metal chemisorbs carbon monoxide at −195°C in a manner similar to iron, except that the ratio of chemisorbed carbon monoxide to the physical monolayer is only 0.65 for the pure cobalt metal. Data on

Table 5. Chemisorption of Carbon Monoxide on Reduced Cobalt Fischer-Tropsch Catalysts

(All data per gram of unreduced catalyst.)

Catalyst	Form [a]	V_m, cc	V_{CO} [b], cc	Complex per g of Complex		$\frac{V_{CO}}{V_m \text{ complex}}$
				V_m, cc	V_{CO}, cc	
Co:ThO_2:MgO:Kg = 100:6:12:200						
89J	P	14.15	3.10	23.92	6.20	0.259
89K	P	14.31	3.80	24.80	7.60	0.306
89K	G	14.19	4.00	24.40	8.00	0.328
Co:ThO_2:MgO = 100:6:12	G	12.06	6.90	12.06	6.90	0.572
Co:ThO_2 = 100:6	G	3.33	1.95	3.33	1.95	0.586
Co:MgO [c] = 100:12	G	8.03	3.70	8.03	3.70	0.461
Co:MgO [d] = 100:8	G	4.17	2.17	4.17	2.17	0.520
Co:Kg [e] = 100:200	G	4.18	0.85	3.28	1.70	0.518
Cobalt basic carbonate	G	0.58	0.36	0.58	0.36	0.632
Cobalt oxide powder		0.73	0.73	0.48	0.48	0.648

[a] G = granules, broken filter cake; P = pellets.

[b] V_{CO} computed from the difference between the total carbon monoxide isotherms and the physical nitrogen at equal relative pressures.

[c] Powdered magnesia.

[d] Precipitated magnesia.

[e] Filter-Cel.

the ratio of chemisorbed carbon monoxide to the physical monolayer of nitrogen for the cobalt-promoter complex, *ie*, the fraction of cobalt metal, are presented in Table 5. For supported and promoted catalysts this ratio was about 0.35, and these samples were the most resistant to sintering during reduction. The ratio for catalysts with only promoters or kieselguhr averaged about 0.50, and for catalysts without promoters and kieselguhr the ratio was 0.63, close to the value for the pure cobalt. X-ray diffraction data were in general agreement with the observed surface areas of the reduced catalysts.

Mercury densities at about 1,140 mm Hg pressure and helium densities were determined on this series of catalysts (Table 6). Under these conditions, mercury will penetrate only pores with openings larger than about 5 microns [32] whereas helium will penetrate all the pores of the catalyst. The volume of pores with openings smaller than 5 microns is given by the difference between the reciprocals of the mercury and helium densities. With granular catalyst containing kieselguhr, it was found that the volume of mercury displaced by the catalyst was nearly equal to the volume of mercury displaced by the kieselguhr plus that displaced by the cobalt-promoter complex, as shown in Figure 13. Thus, the cobalt-promoter complex was deposited only in the pores of the kieselguhr with openings larger than 5 microns. For catalysts containing kieselguhr, the volumes of mercury displaced, per gram of raw (unreduced) catalyst, by the sample in the unreduced or reduced state were equal; however, with unsupported catalysts, the volumes of mercury displaced, per gram of raw catalyst, by the sample in the reduced state were considerably smaller than in the unreduced state. Thus, the catalysts containing kieselguhr did not change in bulk volume during reduction, whereas those without kieselguhr decreased markedly in bulk volume. The pore volumes and surface areas of reduced catalysts containing kieselguhr were larger than those of unsupported catalysts.

The kieselguhr has two functions: first, to maintain the bulk volume and a suitable pore structure especially after sintering or reduction, and, second, to prevent excessive decreases of surface area on sintering or reduction. The bulk kieselguhr has an irregularly packed structure similar to that of a brush-pile. The cobalt-promoter complex is deposited in the pores of the kieselguhr larger than 5 microns in diameter, the bulk volume of the catalyst being that of the kieselguhr. On reduction of the catalyst, the kieselguhr structure remains relatively unchanged, and the cobalt-promoter complex shrinks about the brush-pile structure of the kieselguhr. The presence of the kieselguhr prevents the formation of large crystallites of cobalt.

There is some indication that interaction between cobalt oxide or

TABLE 6. MERCURY AND HELIUM DENSITIES OF UNREDUCED AND REDUCED COBALT CATALYSTS

Catalyst	Form [a]	Unreduced Catalysts					Reduced Catalysts					Mercury Volumes, cc per g of Unredueed Catalyst	
		Densities		Pore Volume, cc per g	Area, sq m per g	Av Pore Diameter $\bar{d}$, [b] Å	Densities		Pore [d] Volume, cc per g	Area, [d] sq m per g	Av Pore Diameter d, Å	Before Reduction	After Reduction
		Hg	He				Hg	He [c]					
Co:ThO_2:MgO:Kg = 100:6:12:200													
89J	P	0.974	2.76	0.66	88.7	297	0.780	3.07	0.95	76.6	500	1.026	1.037
89K	P	1.20	2.77	0.47	88.8	212	1.045	3.08	0.63	77.4	327	0.833	0.768
89K	G	0.611	2.77	1.28	101.1	506	0.537	3.13	1.54	76.8	804	1.635	1.530
89U	P	1.10	2.80	0.55	86.2	255	0.901	3.08	0.79	46.7	672	0.909	0.896
89FF	P	1.295	2.80	0.41	102.9	160	1.138	3.03	0.55	99.0	222	0.772	0.712
Co:ThO_2:MgO = 100:6:12	G	0.781	3.62	1.00	154.8	259	1.057	6.72	0.80	84.1	379	1.280	0.593
Co:Kg = 100:200	G	0.457	2.71	1.75	75.6	926	0.378	3.00	2.31	22.8	4.060	2.189	2.082
Cobalt basic carbonate	G	0.925	3.81	0.82	126.1	293	4.476 [e]	9.00	0.112	4.2	1.070	1.081	0.125

[a] P = pellets (1.6 mm long by 3.2 mm diameter); G = granules, broken filter cake.

[b] Average pore diameters computed from $\bar{d} = 4V/A$, where V is the pore volume and A the surface area per gram.

[c] Helium densities calculated from compositions of reduced eatalysts; 89-type, 3.12; Co:ThO_2:MgO = 100:6:12, 7.79; Co:Kg = 100:200, 3.06; and eobalt basie carbonate, 8.9.

[d] Pore volumes and surfaee area per gram of redueed eatalyst.

[e] This sample wet by mereury.

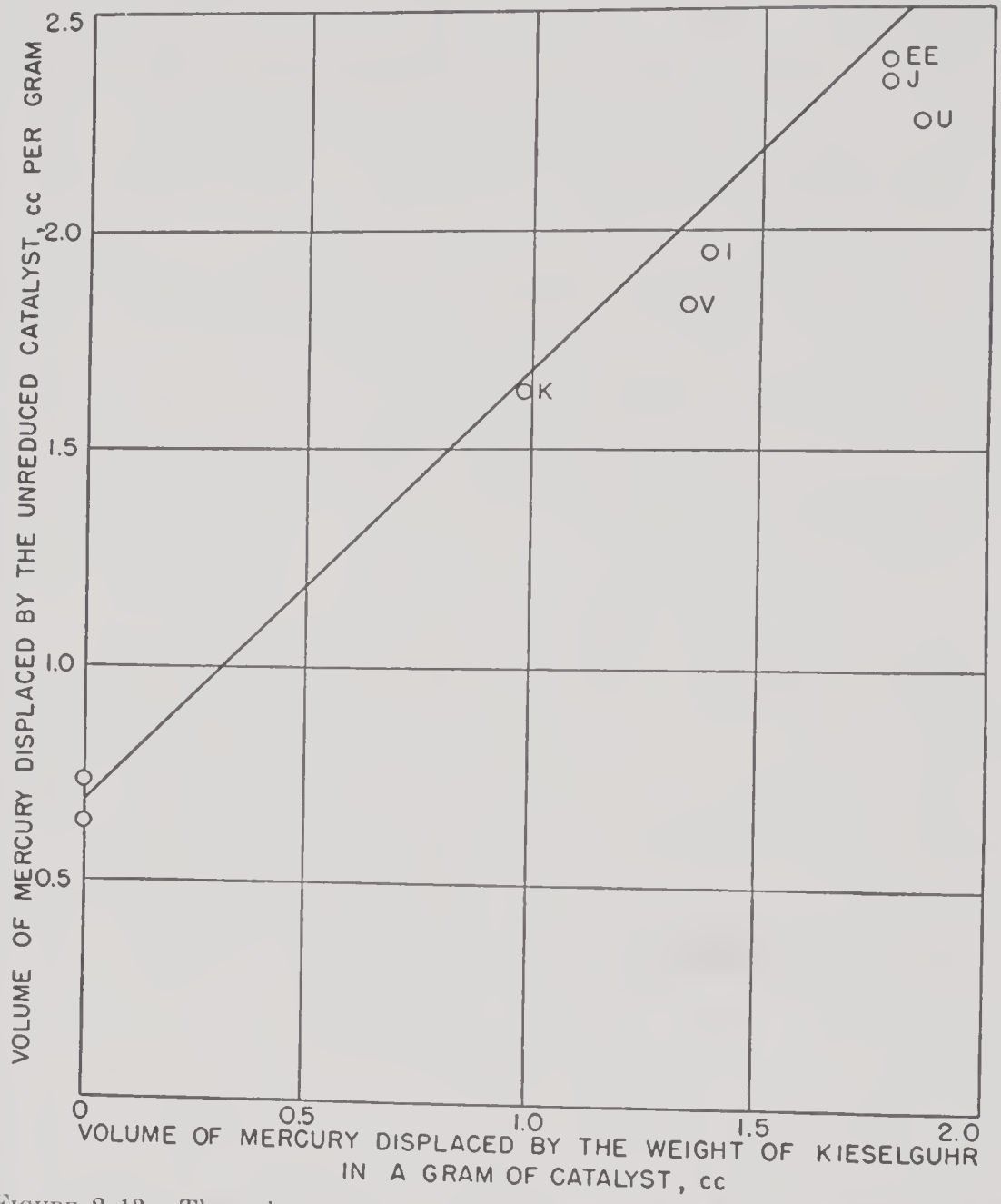


FIGURE 2–13. The volumes of mercury displaced per gram of unreduced cobalt Fischer-Tropsch catalysts of the 89 type in granular form plotted against the volume of mercury displaced by the weight of kieselguhr per gram of catalyst. The mercury-displacement experiments were made at an absolute pressure of 1,140 mm Hg. Reproduced by permission from reference 59.

hydroxide and kieselguhr may occur to a slight extent, but this was not shown by the x-ray diffraction patterns. In nickel catalysts Visser and deLange [5] found evidence of interaction between nickel oxide or hydroxide and kieselguhr to the extent of formation of nickel hydrosilicate bonds as indicated by x-ray diffraction patterns. Teichner [60] reported

[60] S. Teichner, *Compt. rend.*, **227**, 478 (1948).

that the surface area of a nickel-kieselguhr catalyst evacuated at 20°C was 27 sq m per g; after evacuation at 180°C and subsequent reduction at 450°C, the surface area increased to 35 and 67 sq m per g, respectively. All these values are reported per gram of original catalyst. The increase in area on evacuation at 180°C and reduction at 450°C was related to porosity and additional surface area formed by the removal of chemically bound water and carbon dioxide during evacuation and the removal of oxygen during reduction. Teichner [60] postulated that the nickel-hydrosilicate (montmorillonite) structure of these catalysts prevented sintering during evacuation and reduction. The fact that cobalt Fischer-Tropsch catalysts of Anderson, Hall, and Hofer [2] always decreased in area when evacuated at high temperature or when reduced indicated that hydrosilicate bonds, if present, were not of sufficient number to prevent sintering.

THE USE OF TAGGED ATOMS

Valuable information about the mechanisms of catalytic reactions may be obtained from the use of tagged atoms, *ie*, either stable or radioactive isotopes. In general, the procedure is to introduce the tagged atoms as reactants or as part of the catalysts (*eg*, C^{14} as carbide in Fischer-Tropsch catalysts) and to follow the position and amount of these atoms in the reaction products and catalyst as a function of time. Tagged atoms useful in studies of the synthesis of hydrocarbons are listed in Table 7. Included in this table is *para*-hydrogen, which differs

Table 7. Tagged Atoms

Element	Atomic Weight	Radioactive	Method of Analysis
Deuterium	2	No	Thermal conductivity or mass spectrometer
Tritium	3	Yes	Geiger counter
Carbon	13	No	Mass spectrometer
Carbon	14	Yes	Geiger counter
Oxygen	18	No	Mass spectrometer
para-Hydrogen	1	No	Thermal conductivity

from normal hydrogen only by predominance of the *para* spin isomer as compared with the normal equilibrium amounts of the *para* and *ortho* isomers. Analysis by a Geiger counter is very sensitive, and concentrations of 0.1 per cent or less of the radioactive isotope are usually sufficient. On the other hand, the analytical methods for stable isotopes usually require rather high concentrations. Isotopes have slightly mod-

ified chemical and physical properties because of their different mass, these differences being more pronounced for the isotopes of hydrogen in which the ratios of the masses are the greatest. However, for most purposes the properties of the isotopes may be considered identical.

The use of the *para-* to *ortho*-hydrogen interconversion on iron catalysts to examine the nature of the two types of chemisorbed hydrogen

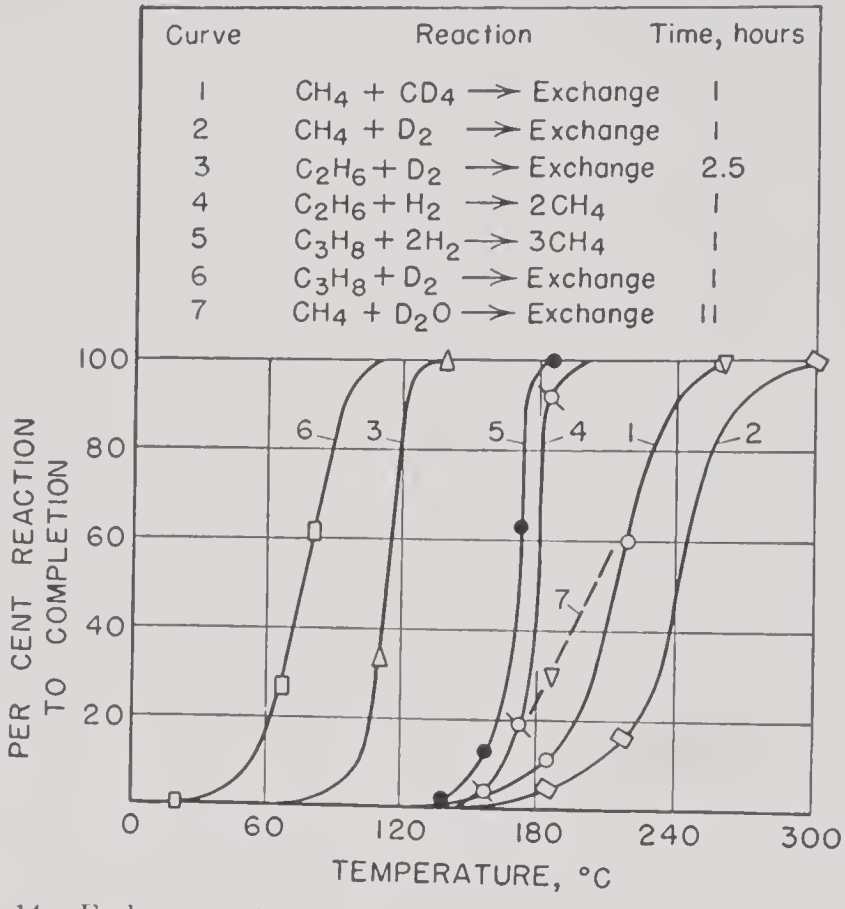


FIGURE 2–14. Exchange and hydrocracking reactions of hydrogen and deuterium and hydrocarbons on a nickel-kieselguhr catalyst. Reproduced by permission from reference 61.

has been described on p 61. The interconversion can occur when hydrogen is adsorbed molecularly on paramagnetic or ferromagnetic surfaces or atomically on any surface. If the interconversion occurs, it indicates that hydrogen molecules can adsorb and escape from such surfaces.

As an example of the use of tagged atoms, the studies of Taylor and coworkers [61] on the rates of exchange of deuterium with hydrogen atoms in methane, ethane, and propane as compared with the rates of hydrocracking of ethane and propane on a nickel-kieselguhr catalyst will be

[61] K. Morikawa, W. S. Benedict, and H. S. Taylor, *J. Am. Chem. Soc.*, **58**, 1,445, 1,795 (1936); K. Morikawa, N. R. Trenner, and H. S. Taylor, *ibid.*, **59**, 1,103 (1937).

discussed. The catalyst was shown to have very little exchangeable hydrogen; thus, any exchange occurred with hydrogen atoms in the hydrocarbons. The extent of exchange or reaction in a given period of time (usually 1 hr) as a function of temperature is shown in Figure 14.

The exchange of CH_4-D_2 required the highest temperatures, considerably higher than required for exchange of hydrogen and deuterium atoms of CH_4-CD_4. The authors suggested that this was due to the relatively strong adsorption of hydrogen and deuterium compared with that of methane. With ethane and propane exchange reactions involving the activation of C—H bonds and hydrocracking reactions requiring activation of C—C bonds occurred; the C—H bond was activated at about 100°C and the C—C bond at about 200°C.

The hydrogenation of ethylene was very rapid on this catalyst at temperatures of −80°C and above, and there was no evidence of breaking of the C−C bond below 138°C. Some exchange of deuterium with the hydrogen atoms of the ethylene was observed, the extent of the exchange reaction increasing with temperature. The ratios of the C—D bonds formed by exchange to the C—D bonds formed by hydrogenation were 0.008 and 0.103 at −80°C and +65°C, respectively.

The authors postulated dissociative adsorption of the type $C_2H_6 \rightarrow C_2H_5 + H$ for exchange reactions and $C_2H_6 \rightarrow 2CH_3$ for the hydrocracking reactions. Some dissociative adsorption of ethylene leading to exchange may occur. Kinetic data indicate that the apparent activation energy for the breaking of a C—C bond was considerably greater than that for a C—H bond.

Kinetics Studies of Catalytic Reactions

EXPERIMENTAL METHODS

A static system is the simplest for studying rates of catalytic gas reactions. If the number of gas molecules changes in the catalytic reaction, the rate may be determined by following the change in pressure with a manometer or pressure gauge connected to the vessel containing the catalyst. This method, which has been used by Craxford and Rideal [62] and Eidus [63] in studies of the Fischer-Tropsch synthesis, is not very satisfactory because the reaction products accumulate and blanket the catalyst. Consequently, there may be considerable uncertainty as to the partial pressures of reactants and products in the immediate vicinity of the catalyst at any time except the beginning of the experiment.

[62] S. R. Craxford and E. K. Rideal, *J. Chem. Soc.*, II, 1,604 (1939).

[63] Y. T. Eidus, *Bull. acad. sci. U.R.S.S.*, **47**, 255 (1944).

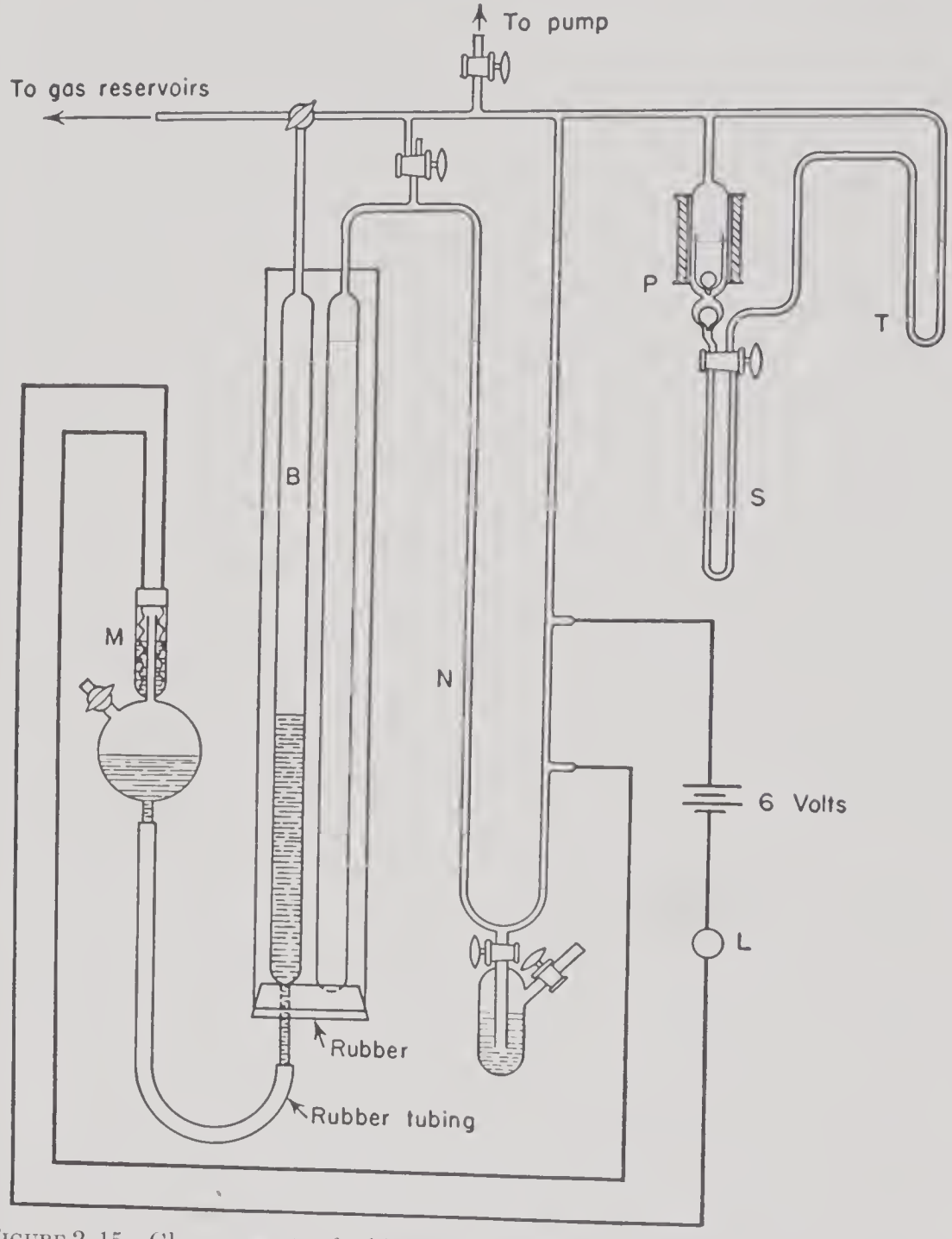


FIGURE 2–15. Glass apparatus for kinetic studies of catalytic reactions. Reproduced by permission from reference 64.

Systems in which the gas flows over the catalyst are more satisfactory than static systems. For studies at atmospheric or lower pressures, the glass system of Weller [64] shown in Figure 15 may be used. Gas is circulated over the catalyst in *S* and through liquid air trap *T* by solenoid-

[64] S. Weller, *J. Am. Chem. Soc.*, **69**, 2,432 (1947).

actuated piston pump *P*. The pressure is kept constant by displacing fresh gas from graduated burette *B* with mercury by the manostating device of Taylor and Strother.[52] A similar apparatus using a magnetically actuated all-glass turbine has been described by Beeck.[20] For studies at higher pressures it is necessary to use metal reactors of either the boiling-liquid-bath or metal-block type. The boiling liquid bath is advantageous in highly exothermic reactions. A typical Downs'-type reactor as used in catalyst testing at the U. S. Bureau of Mines is described in Chapter 3 on p 153. The temperature of the boiling bath is maintained by controlling the pressure at which the liquid boils. Metal-block reactors of the type described by Dodd and Watson [65] are convenient, but the temperature gradient in these reactors is greater than in those with boiling liquid baths, especially for highly exothermic or endothermic reactions.

For simple and unambiguous interpretation of kinetic data of catalytic reactions, the following experimental conditions are desirable:

a. An isothermal bed of catalyst.

b. The changes in partial pressures of reactants and products from the beginning to the end of the catalyst bed should be as small as possible. This may be accomplished by maintaining as low an extent of conversion as the experimental methods permit. If these conditions are met, the average partial pressures may be approximated by one-half of the sum of the outlet and inlet partial pressures of the components.

c. If it is not possible to study the reaction at low extents of conversion, it is desirable to compare rates at a constant but not complete conversion of reactants. Under this condition the average partial pressures of the components may be maintained about constant even though they cannot be computed with great certainty. Although experiments made at complete conversion are of practical value, they provide very little information about the kinetics of the process.

Catalytic activity may be expressed in a number of ways. If the reaction has a simple rate equation, the constants of the equation may be used as an expression of activity. For more complicated reactions, the activities may be expressed as moles of reactants consumed per unit time per unit volume of catalyst, the overall space-time-yield. If the nature and quantity of reaction products vary with conditions of operation, it is necessary to consider the distribution of products as well as the overall activity. In most cases the concept of contact time has no great value in catalytic kinetics, and it is usually preferable to correlate overall space-time-yield and product distribution with the average pressures

[65] R. H. Dodd and K. M. Watson, *Trans. Am. Inst. Chem. Engrs.*, **42**, 263 (1946).

of components and temperature. If the surface area of the catalyst as used in the reaction is known, the activity per unit surface area, the intrinsic activity, may be used.

RATE EQUATIONS FOR CATALYTIC REACTIONS

The determination of rate equations is useful because fundamental information regarding the reaction mechanism may be obtained. The rate equation is also necessary for rational design of reactors. Heterogeneous catalytic reactions may be divided into five steps:

a. Transport of reactants to the catalytic surface.
b. Adsorption of reactants.
c. Reaction of adsorbed reactants.
d. Desorption of products.
e. Transport of products from the catalytic surface.

The problem of evolving rate equations involving all or several of these steps is usually too difficult for a useful solution, and, if possible, the rate is related to the slowest step of the reaction. Rate equations for steps *b*, *c*, and *d* of catalytic reactions have been derived by Schwab, Spence, and Taylor,[66] Glasstone, Laidler, and Eyring,[67] Hougen and Watson,[68] and others. In general, the following assumptions are made:

a. The rate of reaction is proportional to the product of the number of reactant molecules A and B adsorbed on adjacent sites. Unimolecular reactions may proceed by one of two mechanisms: the rate is proportional to the number of adsorbed reactant molecules, in the first case; in the second case, the adsorbed molecule reacts with an adjacent bare site, and the rate is proportional to the product of the number of adjacent bare and occupied sites.

b. The rate of adsorption of component A is assumed to be proportional to the product of the number of bare sites and the partial pressure of A.

c. The rate of desorption of component A is proportional to the number of sites occupied by A. Assumptions *b* and *c* are the same as those used in the derivation of the Langmuir adsorption isotherm.[34]

[66] G. M. Schwab, R. Spence, and H. S. Taylor, *Catalysis*, D. Van Nostrand Co., New York, 1937.

[67] S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill Book Co., New York, 1941.

[68] O. A. Hougen and K. M. Watson, *Ind. Eng. Chem.*, **35**, 529 (1943); *Chemical Process Principles*, vol. III. *Kinetics*, John Wiley & Sons, New York, 1947, Chapter 19.

d. All steps except the rate-controlling one are assumed to proceed at sufficiently rapid rates so that these steps may be regarded as being in equilibrium.

The derivation of a rate equation for a catalytic reaction A + B = R, *eg*, hydrogenation of an olefin, will be outlined. The presentation follows that of Hougen and Watson,[68] and the reader is referred to these authors for further details. For brevity, the symbols used in these equations are summarized below:

r = rate of reaction in terms of space-time-yield, total moles of reactants consumed per unit volume or unit mass of catalyst per unit time.
s = number of equidistant active sites adjacent to each site.
L = total molal adsorption sites per unit volume or mass of catalyst.
c_X = concentration of adsorbed molecules, X, per unit volume or mass of catalyst.
c_L = number of bare sites per unit volume or mass of catalyst.
k and k' = velocity constants of surface reactions in forward and reverse direction, respectively.
k_X and k_X' = velocity constants of adsorption and desorption of component X, respectively.
K = equilibrium constant for the overall reaction.
K_X = adsorption equilibrium constant for component X.

Case 1. Surface reaction rate controlling. The rate of the overall reaction (forward minus reverse) is given by

$$r = \frac{ks}{2L} c_A c_B - \frac{k's}{2L} c_R c_L \tag{12}$$

Since the surface reaction is the slow step, the quantities c_A, c_B, and c_R may be assumed to be in equilibrium with partial pressures of the components at the interface as given by the Langmuir-type equation

$$c_X = p_X K_X c_L \tag{13}$$

The equilibrium constant is related to the adsorption equilibrium constants and rate constants by

$$K = \frac{K_A K_B}{K_R} \frac{k}{k'} \tag{14}$$

and

$$c_L = \frac{L}{1 + K_A p_A + K_B p_B + K_R p_R + K_I p_I} \tag{15}$$

Substituting equations 13, 14, and 15 in 12 gives

$$r = \frac{ksLK_AK_B(p_Ap_B - p_R/K)}{2(1 + p_AK_A + p_BK_B + p_RK_R + p_IK_I)^2} \tag{16}$$

If the equilibrium constant is large and p_AK_A, p_RK_R, and p_IK_I are small with respect to 1, the equation reduces to

$$r = \frac{ksLK_AK_Bp_Ap_B}{2(1 + p_BK_B)^2} = \frac{\alpha Lp_Ap_B}{(1 + \beta p_B)^2} \tag{17}$$

If in addition $p_BK_B \gg 1$, equation 17 reduces to

$$r = \frac{ksLK_Ap_A}{2K_Bp_B} = \frac{\alpha' Lp_A}{p_B} \tag{18}$$

and if $p_BK_B \ll 1$,

$$r = \alpha'' Lp_Ap_B \tag{19}$$

Equation 19 represents the reaction in which none of the components is strongly adsorbed. If component B is moderately strongly adsorbed and the other components weakly adsorbed, equation 17 is the form of the rate expression. Equation 18 represents the case in which component B is very strongly adsorbed.

Case 2. Adsorption of component A rate controlling. The rate of the overall reaction is equated to the rate of the adsorption minus the rate of desorption of component A:

$$r = k_Ap_Ac_L - k_A'c_A \tag{20}$$

where c_A is assumed to be in equilibrium with the partial pressures of B and R at the interface

$$c_A = \frac{p_Rc_LK_A}{p_BK} \tag{21}$$

The term c_L is similar to equation 15 except that c_A is defined by equation 21 and $k_A/k_A' = K_A$. The resulting rate equation is

$$r = \frac{k_AL(p_A - p_R/p_BK)}{1 + p_BK_B + \dfrac{p_RK_A}{p_BK} + p_RK_R + p_IK_I} \tag{22}$$

Again, if K is large, p_RK_R and p_IK_I are much less than 1, and K_A is small, equation 22 becomes

$$r = \frac{k_ALp_A}{1 + p_BK_B} \tag{23}$$

If in addition $p_B K_B \gg 1$ equation 23 becomes

$$r = \frac{k_A L p_A}{p_B K_B} = \frac{\alpha L p_A}{p_B} \tag{24}$$

and if $p_B K_B \ll 1$,

$$r = \alpha' L p_A \tag{25}$$

Equation 25 represents the rate when none of the components is strongly adsorbed, equation 24 when B is strongly adsorbed, and equation 23 when B is moderately adsorbed and the other components weakly adsorbed.

Case 3. Desorption of component R rate controlling. Here the overall rate of reaction is the rate of desorption of R minus its rate of adsorption:

$$r = k_R' c_R - k_R p_R c_L \tag{26}$$

where c_R is assumed to be in equilibrium with components A and B. The resulting equation is

$$r = \frac{k_R L K (p_A p_B - p_R/K)}{1 + p_A K_A + p_B K_B + p_A p_B K_R K + p_I K_I} \tag{27}$$

If K is large, equation 27 reduces to

$$r = \frac{k_R L}{K_R} = k_R' L \tag{28}$$

Included in equations 16, 22, and 27 are terms for component I, which is not directly involved in the reaction. If $p_I K_I$ is large or of the same order of magnitude as the other terms in the denominators, component I is termed a catalyst poison. If adsorbed molecules of I are easily removed by desorption or reaction with other components of the system when it is no longer present in the gas phase, it is termed a reversible or temporary poison, because the activity will again increase to its normal value after removal of component I. If component I is very strongly adsorbed on the surface, it may desorb at a very slow rate, if at all, and the rate will be permanently decreased. Such components are called permanent or irreversible poisons.

Equations 12–31 were derived for molecular adsorption of components. Rate equations for atomic adsorption of one or more components are similar to those for molecular adsorption except that the pressures of the atomically adsorbed components or their equivalent in terms of other pressures are raised to the ½ power (*cf* Hougen and Watson [68]).

In almost every case, the constants of the rate equations must be evaluated from kinetic data, and in many systems it is not possible to establish the rate-controlling mechanism with certainty because different mechanisms may give the same type of rate law. Thus, equations 18 and 24 are identical in their dependencies of the rate on the variables of the reaction. In many cases, studies of the reaction over wide ranges of pressure are informative. At very low partial pressures the terms in the denominators of equations 16, 22, and 27 become less significant with respect to 1.

The rate and equilibrium constants of the overall rate equation are temperature dependent. Rate constants may be expressed as

$$k = Ae^{-\Delta H^{\ddagger}/RT} \tag{29}$$

and equilibrium constants for reactions and adsorption processes as

$$K_X = Be^{-\Delta H_X/RT} \tag{30}$$

where $\Delta H^{\ddagger}$ is the enthalpy of activation and ΔH_X the heat of adsorption of component X. Thus, equation 24 may be expressed as

$$r = \frac{Lk_A p_A}{K_B p_B} = \frac{LAp_A}{Bp_B} e^{-(\Delta H^{\ddagger} - \Delta H_B)/RT} \tag{31}$$

and the observed energy (enthalpy) of activation is $\Delta H^{\ddagger} - \Delta H_B$. Since heat is evolved in adsorption processes, ΔH_B is negative and the observed energy of activation is greater than that of the actual rate process by ΔH_B.

If the form of the rate equation is not known or if it is very complicated, overall apparent activation energies that have usefulness may be estimated from the rates of reactions at various temperatures with the average partial pressures of the reactants and products maintained approximately constant. This may be achieved by comparing the rates either at constant extents of conversion or at very low conversions.

The derivation of rate equations of the type of equations 12–31 involves assumptions that are not strictly correct in that the catalytic surface is assumed to be uniform with respect to heat of adsorption and activation energies. There is considerable evidence to indicate that these quantities may vary considerably with the extent of coverage of the surface with like and unlike molecules. For this reason the heat and activation energy terms are usually evaluated from the kinetic data and represent average values of these terms for the concentrations of adsorbed molecules found in the reaction. It is possible to derive more exact equations involving variations of surface activity, but in most

cases the rate equations become too complicated for their practical application to catalytic kinetic data.

Mass transfer to the catalyst surface is of two types: (*a*) mass transfer to the catalyst particle, or (*b*) mass transfer within the pores of the particle. If transfer to the particle is the rate-determining step, the overall activation energy of the process may be expected to be of the same order of magnitude as those for diffusional processes, which are usually less than 5 kcal per mole. Chilton and Colburn [69] and Gamson, Thodos, and Hougen [70] have developed equations for this type of mass transfer in terms of Reynolds and Schmidt numbers.

Mass transfer within the pores of a catalyst is rather complicated. For example, consider a reaction occurring within a pore whose length is very much greater than its diameter. If there is no change in number of molecules in the reaction, the rate of diffusion of reactants in the pore is proportional to the concentration gradient along its length. The concentration gradient is, in turn, determined by the number of molecules reacting along the walls of capillary. If the number of molecules decreases or increases in the reaction, there is a net flow into or out of the pore, respectively, in addition to mass transfer by diffusion. If the reaction is very rapid, molecules of reactant can move only a very short distance before reacting, and the fraction of the pore wall that is accessible or effective is small. Conversely, for slow reactions a greater fraction of the pore wall is accessible. Increasing the temperature of the system increases the reaction rate and may decrease the depth to which the reactant can penetrate (the rate of diffusion increases only slightly with temperature); at the higher temperature a smaller fraction of the pore surface will be accessible. Hence, the temperature coefficient of the reaction in the pore may be smaller than on a plane surface.

Thiele [71] presented a mathematical analysis of several simple types of reactions occurring in pore systems. The effectiveness factor, the ratio of the rate of reaction per unit total surface area on a catalyst of a given pore structure to the rate per unit area of a non-porous surface of identical composition, was computed in terms of the modulus

$$d\sqrt{\frac{k}{Dr}}$$

where d is the particle diameter, k the activity per unit surface area, D

[69] T. H. Chilton and A. P. Colburn, *Ind. Eng. Chem.*, **23**, 913 (1931).

[70] B. W. Gamson, G. Thodos, O. A. Hougen, *Trans. Am. Inst. Chem. Engrs.*, **39**, 1 (1943).

[71] E. W. Thiele, *Ind. Eng. Chem.*, **31**, 916 (1939).

the diffusion coefficient, and r the average pore radius. The variation of the effectiveness factor with modulus is shown in Figure 16. With increasing values of the modulus the effectiveness factor decreases, and at high values of the modulus the slope of the curve approaches -1 on the log-log plot.

For the simple reactions considered by Thiele, it may be shown that, for values of the effectiveness factor near unity, the activation energy for a reaction on the porous catalyst is the same as that observed on a plane surface. As the effectiveness factor decreases, the observed activation

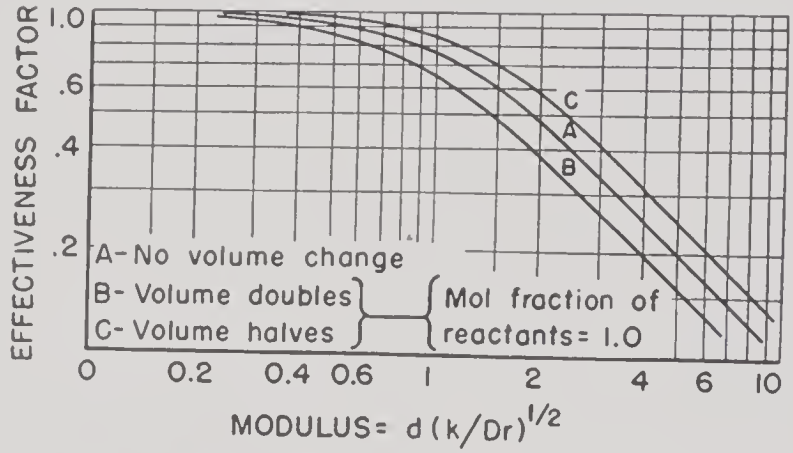


FIGURE 2–16. Plots of effectiveness factor against Thiele's modulus. Reproduced by permission from reference 71.

energy becomes less than that of the reaction on a plane surface, approaching as a limit an activation energy equal to 50 per cent of that observed on a plane surface. Thiele's analysis of simple reactions in simple pore systems is very instructive, and, in the absence of similar relationships for more complicated systems, may be considered as a first approximation for any type of reaction. Empirical methods of evaluating kinetic data using Thiele's curves have been proposed by Hougen and Watson.[68]

Thus, it should be noted that in many cases diffusion in the pores of a catalyst is related to the rate of reaction at the catalyst surface in a manner which does not allow the reaction to be classed as one controlled entirely by either surface processes or diffusion. For these cases, in the use of equations 12–31, Hougen and Watson [68] substitute the effective number of adsorption sites, L', for L, where L' is equal to L multiplied by the effectiveness factor. The effective number of sites, L', is not a constant, but has the same temperature dependence as the effectiveness factor.

EXAMPLES OF CATALYTIC REACTIONS

In this section the kinetics of the hydrogenation of olefins and the synthesis of ammonia and alcohols will be discussed. These reactions were chosen because they have been studied thoroughly and because of their similarity in some respects to the Fischer-Tropsch synthesis.

Hydrogenation of Olefins

There are two types of reactions between olefins and hydrogen. The first, which occurs at low temperatures, is the addition of hydrogen at the double bond, while the second, occurring at higher temperatures, is hydrocracking to saturated hydrocarbons. Both reactions are thermodynamically favorable below 400°C. The temperature at which hydrocracking reactions become important depends upon the catalyst. Thus, a copper catalyst hydrogenates ethylene to ethane at temperatures as high as 250°C or 300°C, whereas a nickel catalyst hydrocracks ethylene to methane at temperatures below 100°C.

Pease [72] studied the hydrogenation of ethylene on copper catalysts at 0°–250°C in a static glass system. At about 0°C the rate was given by

$$r = \frac{\alpha p_{H_2}}{p_{C_2H_4}} \tag{32}$$

with the activation energy in this range being about 13 kcal per mole. At 100°C the rate followed the equation

$$r = \alpha' p_{H_2} \tag{33}$$

the activation energy again being 13 kcal per mole. At 200°C the rate law was

$$r = \alpha'' p_{H_2} p_{C_2H_4} \tag{34}$$

and the activation energy was 6.0 kcal per mole. Equations 32 and 34 may correspond to the limiting forms of equation 17, assuming a surface reaction between hydrogen and ethylene as the rate-determining step. The value of the adsorption equilibrium constant for ethylene in the denominator of equation 17 should decrease exponentially with temperature, and at an intermediate temperature the rate equation may be approximated by equation 33. Equations 32 and 33 are also the same as those derived when it is assumed that the rate of adsorption of hy-

[72] R. N. Pease, *J. Am. Chem. Soc.*, **45**, 1,196, 2,235 (1923); **47**, 1,235 (1925); **47**, 2,503 (1927).

drogen is the rate-determining step and that ethylene is strongly adsorbed at the lower temperature.

Ethylene and hydrogen are strongly adsorbed at 0°C. The hydrogen adsorption at this temperature is very probably chemisorption, but that of ethylene may be, at least partially, physical adsorption because 0°C is below the critical temperature of ethylene (9.7°C). Carbon monoxide is more strongly adsorbed than hydrogen or ethylene, and small amounts of carbon monoxide severely poison the catalyst for hydrogenation of ethylene. Thus, the catalyst adsorbed about 1 cc of hydrogen, 2 cc of ethylene, and 5 cc of carbon monoxide at pressures of 1 mm Hg. However, 0.05 cc of carbon monoxide decreased the activity to 12 per cent of its original value, although not more than 1 per cent of the surface was covered with carbon monoxide. This is evidence for the concept of inhomogeneity of catalyst surfaces.

Emmett and Gray [73] studied the low-temperature (−20° to +20°C) hydrogenation of ethylene, propylene, and 2-butene on pure iron catalysts and promoted iron synthetic-ammonia catalysts, using a glass system including a glass turbine for circulating gases as described in a previous section (p 76). For all the olefins the rate was approximately proportional to the partial pressure of hydrogen. The respective hydrogenation rates increased slightly with increased partial pressure of ethylene, decreased slightly with partial pressure of propylene, and were independent of the partial pressure of 2-butene. It was shown that polymerization reactions did not occur to an appreciable extent in any case. The reaction rate of 2-butene was not decreased by physically adsorbed butene until a layer of about 1-mm thickness was present on the catalyst. The data indicated that the rate-determining step is either the adsorption of hydrogen or its reaction with olefin. Emmett and Gray suggested that physical adsorption of the olefin is involved in its hydrogenation, as indicated previously by Hansford and Emmett.[74] The energies of activation of hydrogenation of ethylene, propylene, and 2-butene were 9.7, 7.4, and 6.5 kcal per mole, respectively. The data indicated that aluminum oxide as a promoter had little effect on the activity per unit surface area, but potassium oxide in excess of an alumina to potassium oxide ratio of 4 decreased the rate of reaction, this effect being quite marked in the case of ethylene.

Beeck, Wheeler, and coworkers [20,75] studied the hydrogenation of ethylene at 0°C on evaporated pure metal films of various group eight (of the periodic table) and other metals. These experiments were care-

[73] P. H. Emmett and J. B. Gray, *ibid.*, **66**, 1,338 (1944).
[74] R. C. Hansford and P. H. Emmett, *ibid.*, **60**, 1,185 (1938).
[75] O. Beeck, *Revs. Modern Phys.*, **17**, 61 (1945); *Rev. Chem. Progress*, **8**, 105 (1947).

fully planned and executed and are the most complete and unambiguous of any catalytic reaction studied to date. The reaction was studied in an all-glass system in which the reacting gases were circulated by a glass turbine. The reaction was strictly first order with respect to hydrogen, and the rate was somewhat decreased by high ethylene to hydrogen ratios. Surface areas were determined by physical adsorption of an inert gas, and activities were expressed in terms of the first-order rate constant divided by surface area, the intrinsic activity. For all the metals studied the activation energy of the hydrogenation was 10.7 kcal per mole.

The evaporated catalyst films were prepared with extreme care, using high-vacuum techniques, from pure and carefully degassed metal wires. Thus, the catalyst films were free from impurities normally introduced in the preparation and reduction of metal catalysts, such as adsorbed ions, hydrogen, or residual oxygen. Films evaporated in high vacuum were highly porous; *eg*, a nickel film weighing 50 mg and having an apparent surface of 30 sq cm had a surface area of about 5,000 sq cm. This film gave an electron diffraction pattern of randomly oriented aggregates of crystallites. Films evaporated in an inert atmosphere such as 1 mm Hg of argon gave an electron diffraction pattern of completely oriented metal in which the 110 plane of the face-centered cubic nickel lattice was oriented parallel to the glass surface. The surface areas were about twice as large as the unoriented, high-vacuum films. The intrinsic activity of the oriented films was about five times that of unoriented ones. Rate measurements were made on a series of metals as shown in Figure 17, in which the intrinsic activity is plotted against the lattice distance of the metals. The data fall on a smooth curve, with a maximum for rhodium with a spacing of 3.75 Å, which approximates the distance between hydrogen atoms in opposite methyl groups of ethane.

The dependencies of the rate on partial pressure suggest as rate-determining steps either the rate of reaction of adsorbed molecular hydrogen and adsorbed ethylene with moderately strong adsorption of ethylene (equation 18) or the rate of adsorption of hydrogen with weak adsorption of ethylene (equations 24 and 25). These mechanisms were considered critically in the light of the following observations:

1. The rate of adsorption of hydrogen was instantaneous in this range, and the activation energy of the adsorption was about zero.

2. Adsorbed ethylene dissociated to form acetylenic complexes and hydrogen atoms. These acetylenic complexes act as a poison to the hydrogenation.

The following mechanism was proposed: The rate of removal of acetylenic complexes is proportional to partial pressure of hydrogen and

inversely proportional to that of ethylene. The area available to hydrogen adsorption (*ie*, the area not covered by acetylenic complexes) also has this dependence, and the area of the surface not occupied by acetylenic complexes is always covered by adsorbed hydrogen atoms. The rate of hydrogenation is proportional to the fraction of the surface covered by hydrogen and the partial pressure of ethylene; this implies that physically held ethylene reacts with the chemisorbed hydrogen.

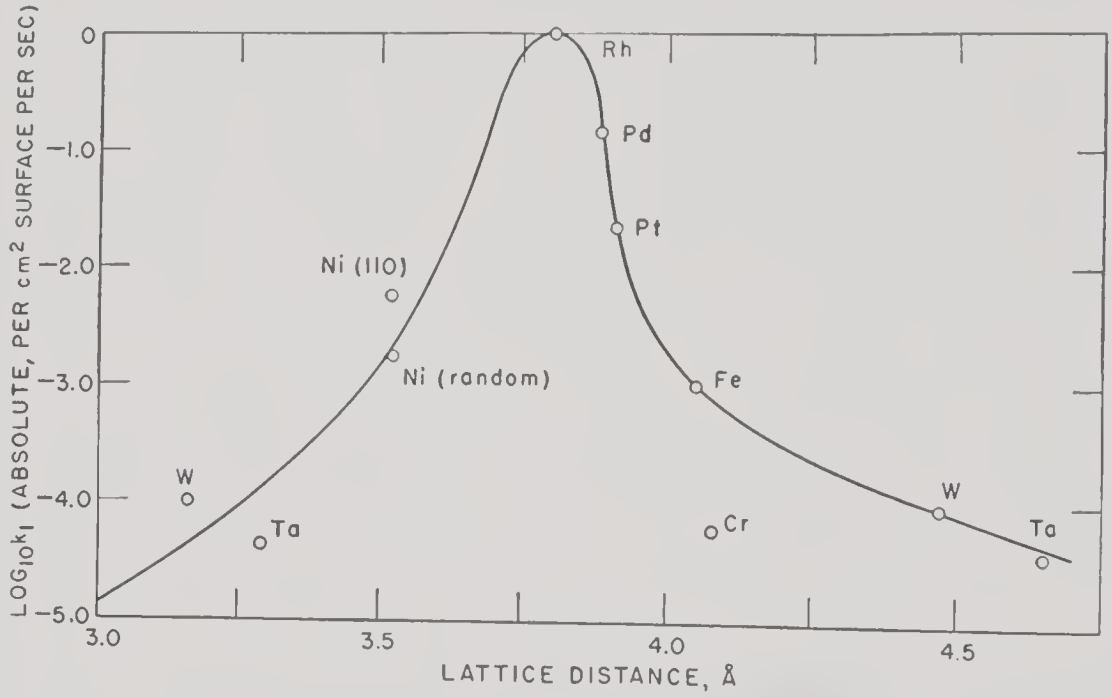


FIGURE 2–17. Activity of metal films in the hydrogenation of ethylene as a function of lattice distance. Reproduced by permission from reference 75.

Thus, the overall rate of reaction is proportional to the pressure of hydrogen. Equations 18, 24, and 25 do not lead to this interpretation.

The rate constant k for a catalytic reaction may be expressed in the form given by Eyring: [67]

$$k = \frac{\kappa T}{h} e^{\Delta S\ddagger/R} e^{-\Delta H\ddagger/RT} \tag{35}$$

where κ and h are Boltzmann and Planck constants, and $\Delta S\ddagger$ and $\Delta H\ddagger$ the entropy and energy (enthalpy) of activation. The rate constants in Figure 17 differ by as much as 10^4. Since the energy of activation is the same for this reaction on all the metal films, the observed activities must be due to variation of the entropy of activation, and these entropies may be controlled by the lattice parameters or "geometry" of the surface as related to the "geometry" of the reactants. Recently, Boudart [75a]

[75a] M. Boudart, *J. Am. Chem. Soc.*, **72**, 1,040 (1950).

suggested that the entropy of activation may not depend upon the lattice dimensions but upon the electronic structure of the metals, especially the configuration of the *d*-shells (see p 5). According to Pauling's theory of metals [75b] the lattice spacing is a function of the *d*-character of the metallic bond. For the data of Figure 17, Boudart found that the logarithm of activity was a steadily increasing function of the per cent *d*-character of the bonds of the metals.

Carbon monoxide was strongly chemisorbed on these films at room temperature and was an effective poison for the hydrogenation of ethylene. In contrast to the data of Pease [72] on poisoning of copper catalysts, in which small quantities of carbon monoxide greatly decreased the activity, the decrease in activity of the evaporated films was directly proportional to the amount of chemisorbed carbon monoxide. These data indicate that the surface of the evaporated films has uniform activity. The difference in the poisoning of the metal films and granular precipitated and reduced catalysts may be due to differences in the geometry of the atoms or to the difference in pore structure (*ie*, accessibility of the surface).

Tschernitz, Bornstein, Beckman, and Hougen [76] studied the kinetics of the hydrogenation of co-dimer, mixed iso-octenes, on a supported nickel catalyst in a metal-block reactor. The data were analyzed by the methods of Hougen and Watson. Seventeen possible rate equations were written for the reaction, and the constants of these equations were determined by the method of least squares for a number of experiments in which the partial pressures of hydrogen, co-dimer, and hydrogenated co-dimer were varied at temperatures of 200°, 275°, and 325°C. All the rate equations except two were eliminated because some of their constants had large negative values where only positive values were possible and other constants that should be zero had large positive or negative values. The two acceptable equations agreed with the experimental data with average deviations of ±17 per cent and ±34 per cent. The equation with the smallest average deviation, corresponding to a reaction mechanism in which the rate-controlling step is a surface reaction between adsorbed co-dimer and adsorbed molecular hydrogen, is given by

$$r = \frac{\alpha K_H K_U p_H p_U}{[1 + K_H p_H + K_U p_U + K_S p_S]^2} \tag{36}$$

where the subscripts H, U, and S represent hydrogen, co-dimer, and

[75b] L. Pauling, *Proc. Roy. Soc.* (*London*), **A196**, 343 (1949).

[76] J. L. Tschernitz, S. Bornstein, R. B. Beckman, and O. A. Hougen, *Trans. Am. Inst. Chem. Engrs.*, **42**, 883 (1946).

hydrogenated co-dimer, respectively, and α is the product of the effective surface area times the surface rate constant. At 275°C with the pressures expressed in atmospheres the values of the adsorption equilibrium constants are $K_H = 0.246$, $K_U = 0.503$, and $K_S = 0.065$. At pressures lower than 0.1 atm the rate law approaches equations 19 and 34, observed by Pease for the hydrogenation of ethylene on copper catalysts at 200°C.

The temperature dependencies of the adsorption equilibrium constants and α were expressed as

$$K_X = e^{\Delta S/R} e^{-\Delta H/RT} \tag{37}$$

$$\alpha = e^{B/R} e^{-\Delta H\ddagger/RT} \tag{38}$$

where ΔH and ΔS represent enthalpies and entropies of the adsorption and rate process. The values of these quantities were found to be as follows:

	ΔH	ΔS
Hydrogen	− 3,110	− 8.49
Co-dimer	− 940	− 3.08
Hydrogenated co-dimer	−13,700	−30.46
α	+ 1,740 [a]	+ 2.82 [b]

[a] Enthalpy of activation.

[b] A constant related to entropy of activation.

The high values of the heat and entropy of adsorption terms for hydrogenated co-dimer are unexpected. It should be noted that the product of adsorption constants K_H and K_U decreases more rapidly than α increases with temperature, so that the rate of hydrogenation decreases with temperature.

The Synthesis of Ammonia on Iron Catalysts

The reaction of hydrogen and nitrogen is not favorable thermodynamically, as shown by the data of Larson and Dodge: [77]

Temperature, °C	350	400	450	500
$K_p = \frac{P_{NH_3}}{P^{1/2}_{N_2} P^{3/2}_{H_2}}$	0.0273	0.0129	0.00676	0.00386

To obtain an appreciable conversion per pass, it is necessary to use high pressures; for example, at 450°C the percentage of ammonia in equilib-

[77] A. T. Larson and R. L. Dodge, *J. Am. Chem. Soc.*, **45**, 2,918 (1923); A. T. Larson, *ibid.*, **46**, 367 (1924).

rium with $3H_2:1N_2$ is 5.87 per cent at 30 atm and 16.43 per cent at 100 atm. Nitrides of iron such as Fe_4N and Fe_2N can be formed by treating iron with pure ammonia at temperatures of the synthesis, and this nitrogen can be removed as ammonia by pure hydrogen. Emmett, Hendricks, and Brunauer [78] have computed the dissociation pressure of Fe_4N from the equilibrium constant of the reaction $8Fe + 2NH_3 = 2Fe_4N + 3H_2$. At 420°C and above, the dissociation pressure of Fe_4N is greater than 4,000 atm. Thus, bulk-phase nitrides of iron cannot be formed from nitrogen and are not intermediates in the ammonia synthesis.

The development of the fused magnetite catalysts of Larson and coworkers [79] illustrates the effect of promoters on catalyst activity; some of these data are presented in Table 8. Addition of difficultly reducible

Table 8. Effect of Promoters on Fused Iron Catalysts, 450°C and Space Velocity of $3H_2 + 1N_2$ of 5,000 [a]

(Equilibrium percentages of ammonia are 5.81 at 30 atm and 16.43 at 100 atm.)

Quantity of Promoters, per cent	Ammonia Formed, per cent	
	30 atm	100 atm
None (pure iron)	3.30	5.49
0.20 K_2O	1.57	3.43
1.01 Al_2O_3	5.02	9.00
0.35 K_2O + 0.84 Al_2O_3	5.82	13.60
0.61 ZrO_2	4.88	7.72
0.96 K_2O + 0.75 ZrO_2	5.43	12.73
0.51 SiO_2	4.67	7.49
0.57 K_2O + 0.75 SiO_2	5.33	10.90
1.71 W	3.51	4.83
0.33 K_2O + 0.59 W	4.53	10.50
0.51 Mn	4.60	7.42
0.30 K_2O + 0.99 Mn	3.72	8.59
1.04 Ni	3.24	5.31
0.33 K_2O + 0.37 Ni	2.00	4.65

[a] Reference 79.

oxides to iron increased the catalytic activity, whereas reducible oxides such as those of nickel and copper decreased the activity. Catalysts containing potassium oxide and difficultly reducible oxides were considerably more active, especially at 100 atm, than those containing only

[78] P. H. Emmett, S. B. Hendricks, and S. Brunauer, *ibid.*, **52**, 1,456 (1930).

[79] A. T. Larson and A. P. Brooks, *Ind. Eng. Chem.*, **18**, 1,305 (1926).

the difficultly reducible oxide. The presence of alkali decreased the activity of pure iron catalysts or those containing easily reducible oxides. The difficultly reducible oxides act as structural promoters, as described in a previous part of this chapter (pp 42 and 64).

The promoter action of potassium oxide in conjunction with a difficultly reducible oxide has been postulated to consist in accelerating the rate of desorption of ammonia from the catalyst,[3] possibly from the difficultly reducible oxide. Kagan, Morozov, and Podurovakaya [80] found that ammonia was strongly adsorbed on alumina from 600° to 700°C. Addition of potassium oxide decreased the adsorption of ammonia. The data in Table 8 indicate that the best promoters for iron catalysts are alumina, zirconia, or silica together with potassium oxide.

In the United States, synthetic-ammonia catalysts are usually prepared by fusing a suitable magnetite powder (or ore) together with promoters in an electric resistance furnace. This method of preparation has been described by Larson and Richardson [81] and Bridges, Pole, Beinlich, and Thompson.[82]

Chemisorption of nitrogen on iron catalysts. Adsorption of hydrogen on iron catalysts (p 58) occurs rapidly at synthesis temperatures and very probably is not a rate-determining step in reaction. However, nitrogen chemisorbs considerably more slowly than hydrogen. Emmett and Brunauer [83] studied the chemisorption of nitrogen at 273°–450°C on promoted and pure iron catalysts. At 400°C the rate of adsorption was of the same order as the rate of synthesis of ammonia. The energy of activation of the adsorption was 16.0 kcal per mole, and the heat of adsorption 35.0 kcal per mole. The chemisorbed nitrogen was readily removed by hydrogen to form ammonia at 200°C. The same amount of nitrogen was adsorbed from an NH_3-H_2 mixture having, on the basis of the equilibrium constant for the formation of ammonia, the same partial pressure of nitrogen as in experiments with pure nitrogen.

Catalyst poisoning with water vapor. Almquist and Black [84] showed that appreciable amounts of oxygen were retained by catalysts when treated with $3H_2$ to $1N_2$ gas containing 0.016 per cent water vapor at 444°C. Equilibrium data show that massive iron is not oxidized by a water vapor-hydrogen mixture until the water vapor exceeds 16 per cent. The amount of water taken up was equivalent to the oxidation of

[80] M. Y. Kagan, N. M. Morozov, and O. M. Podurovakaya, *J. Phys. Chem. (U.S.S.R.)*, **8**, 677 (1936); *C.A.*, **31**, 2,078.

[81] A. T. Larson and C. N. Richardson, *Ind. Eng. Chem.*, **17**, 971 (1925).

[82] G. L. Bridges, G. R. Pole, A. W. Beinlich, Jr., and H. L. Thompson, *Chem. Eng. Progress*, **43**, 291 (1947).

[83] P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, **56**, 35 (1934).

[84] J. A. Almquist and C. A. Black, *ibid.*, **48**, 2,814 (1926).

about 1 iron atom in 400. These authors concluded that active atoms on the surface have a greater tendency to oxidize, and that these are probably the same iron atoms that can chemisorb nitrogen at pressures considerably lower than those required to form bulk-phase Fe_4N. The chemisorption of water at atmospheric and 100 atm pressure [84, 85] seriously inhibited the activity of the catalysts in the ammonia synthesis. However, the poisoning was only temporary, for when the water vapor was removed from the gas stream, the catalysts gradually regained their initial activity.

Kinetics of the decomposition of ammonia. The catalytic decomposition of ammonia can be studied easily at atmospheric pressure because the equilibrium concentration of ammonia is quite low. On most iron catalysts the rate may be expressed as

$$r = \frac{\alpha p^{n}_{NH_3}}{p^{m}_{H_2}} \tag{39}$$

where $n \lessgtr 1$ and m is usually less than 1. Winter [86] found n to be about 1 and $m = \frac{3}{2}$ for an iron catalyst supported on alumina. Love and Emmett [87] found for the decomposition of ammonia on doubly promoted catalysts that $m = 0.67$ and $n = 0.9$; the activation energy was 45.6 kcal per mole (Figure 18). With singly promoted catalysts the kinetics were quite unusual, as illustrated in Figure 19. In the region between 400° and 425°C the rate was approximately proportional to the hydrogen pressure, inversely proportional to the pressure of ammonia, and independent of the temperature (very low activation energy). Above and below the horizontal portions, the activation energies were 20–30 kcal per mole in various experiments, and the dependence of rate on partial pressures approached that of the doubly promoted catalyst. It was postulated that the horizontal portion of the rate curve may be related to accumulation of NH or NH_2 groups on the surface, causing another reaction step to become rate controlling.

Equations of Temkin and Pyzhev applied to the rates of decomposition and synthesis of ammonia. The rate equation for the decomposition of ammonia could not be related to the reaction mechanism that seems most plausible, *ie*, that the slow step is the escape of nitrogen molecules from the surface, according to equations of the type described on pp 77–82. Temkin and Pyzhev [88] proposed some unusual

[85] S. Brunauer and P. H. Emmett, *ibid.*, **52**, 2,682 (1930).
[86] E. Winter, *Z. physik. Chem.*, **B13**, 401 (1931).
[87] K. S. Love and P. H. Emmett, *J. Am. Chem. Soc.*, **63**, 3,297 (1941).
[88] M. Temkin and V. Pyzhev, *Acta Physicochim.* U.R.S.S., **12**, 327 (1940).

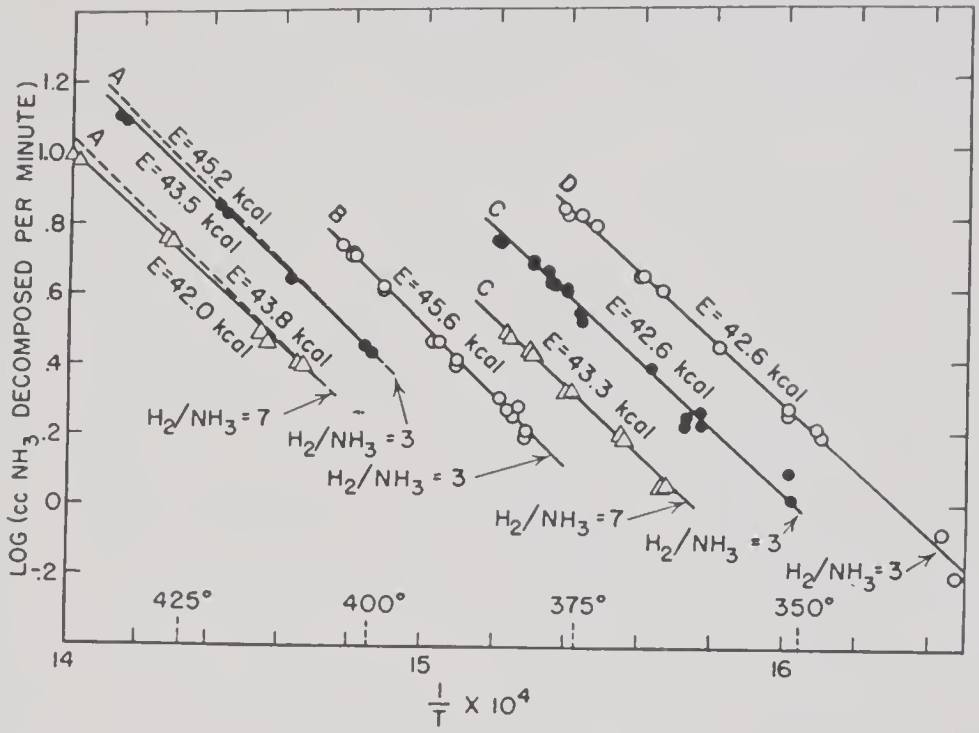


FIGURE 2–18. Temperature dependence of rate of ammonia decomposition on catalyst 931 ($Fe\text{-}Al_2O_3\text{-}K_2O$). Dotted curves have been corrected for small change in composition of the gas in passing through catalyst. Reproduced by permission from reference 87.

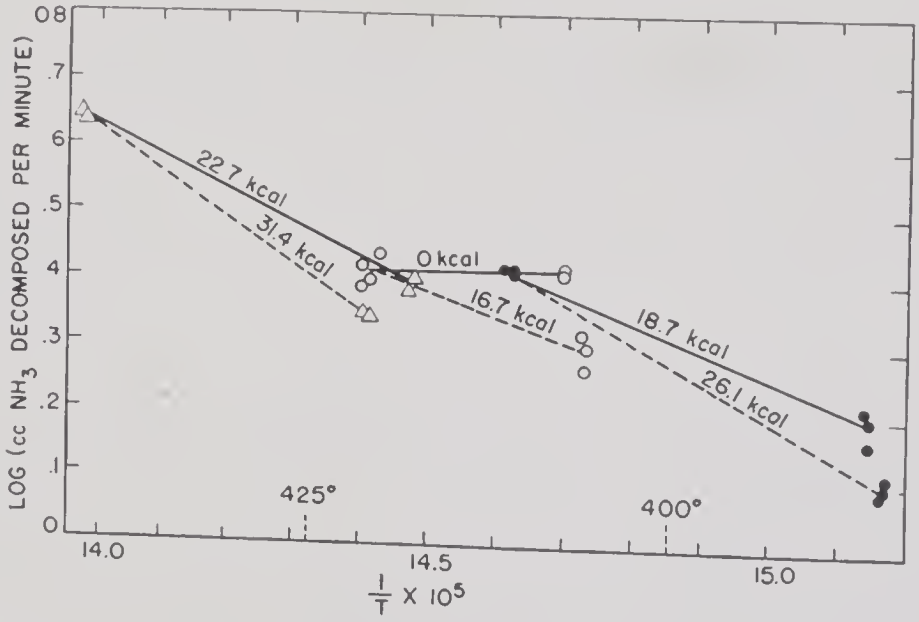


FIGURE 2–19. Temperature dependence of the rate of ammonia decomposition on iron catalyst ($Fe\text{-}Al_2O_3$). Dotted lines represent data for decreasing temperature; solid lines data for increasing temperature. Reproduced by permission from reference 87.

equations for the interaction of nitrogen and iron which have apparently solved the problem. These equations are:

$$\theta = \frac{1}{f} \ln a_0 p'_{N_2} \tag{40}$$

$$r = k_a P_{N_2} e^{-g\theta} \tag{41}$$

$$w = k_d e^{h\theta} \tag{42}$$

where θ = fraction of the surface covered by adsorbed nitrogen.
p'_{N_2} = equilibrium nitrogen pressure.
r = rate of adsorption of nitrogen.
P_{N_2} = instantaneous nitrogen pressure.
w = rate of desorption of nitrogen.
k_a, f, a_0, k_d, and g are constants.

The adsorption of nitrogen from an ammonia-hydrogen mixture was assumed to be the same as it would be with a partial pressure of nitrogen equal to the pressure of nitrogen in equilibrium with the ammonia-hydrogen mixture. Thus, the equivalent nitrogen pressure is equal to $p^2_{NH_3}/Kp^3_{H_2}$, and

$$\theta = \frac{1}{f} \ln a_0 p'_{N_2} = \frac{1}{f} \ln a_0 \frac{p^2_{NH_3}}{p^3_{H_2} K} \tag{43}$$

Then, if the slow step is the escape of nitrogen molecules from the surface, the rate of decomposition of ammonia is given by the rate of desorption of nitrogen molecules:

$$\begin{aligned} w &= k_d e^{-[(h/f) \ln a_0 p^2_{NH_3}/p^3_{H_2} K]} \\ &= k_2 \left(\frac{p^2_{NH_3}}{p^3_{H_2}} \right)^{h/f} \end{aligned} \tag{44}$$

If h/f is assumed to be $\frac{1}{2}$, equation 44 reduces to the rate expression found by Winter,[86] and if $h/f = 0.3$, the equation is that of Love and Emmett.[87]

The rate of synthesis is assumed to be equal to the rate of adsorption of nitrogen:

$$\begin{aligned} r &= k_a P_{N_2} e^{-[(g/f) \ln a_0 p^2_{NH_3}/K p^3_{H_2}]} \\ &= k_1 P_{N_2} \left(\frac{p^3_{H_2}}{p^2_{NH_3}} \right)^{g/f} \end{aligned} \tag{45}$$

From a balance of the rates of synthesis and decomposition at equilibrium, $g/f = h/f$. With h/f assumed to be equal to $\frac{1}{2}$, the rate equation for the synthesis becomes

$$\frac{1}{2} r_{NH_3} = k_1 \frac{p_{N_2} p_{H_2}^{1.5}}{p_{NH_3}} - k_2 \frac{p_{NH_3}}{p_{H_2}^{1.5}} \tag{46}$$

It should be noted that the equations of Temkin and Pyzhev apply satisfactorily only to the kinetics on doubly promoted catalysts.

Temkin and Pyzhev [88] and Emmett and Kummer [89] applied equation 46 to atmospheric- and high-pressure synthesis of ammonia on doubly promoted iron catalysts. The calculations are too detailed for the present discussion, and the reader is referred to the paper of Emmett and Kummer.[89] The rate equation was tested by computing the value of a constant that is proportional to the term k_d of the rate of desorption equation 44. The calculated values of this rate constant at a given temperature were remarkably constant over wide ranges of pressures, gas flow, and composition; for example, the kinetic data of Emmett and Kummer cover space velocities of 25,000–125,000 per hr, pressures of 33.3–100 atm, temperatures from 370° to 450°C, and gas compositions of $3H_2 + 1N_2$, $1H_2 + 1N_2$, and $1H_2 + 3N_2$. In general, the rate constants at a given pressure and temperature varied by only 20–30 per cent over these wide ranges of composition and flow; however, the constants at a given temperature decreased about two-fold from 33.3 to 100 atm. The temperature dependence of the rate constant should be that of the decomposition of ammonia; the activation energies for the ammonia decomposition calculated *from the synthesis data* varied from 45,000 to 53,000 kcal per mole, comparing favorably with the direct measurement of this activation energy by Love and Emmett [87] of 46.5 ± 2.0 kcal per mole. At least a part of the variation of the rate constant with pressure may be attributed to the fact that partial pressures rather than fugacities were used in all the calculations.

Thus, the equations of Temkin and Pyzhev [88] have been shown to be essentially correct for both the synthesis and decomposition of ammonia, and the tests of these equations have been as severe as those applied to any catalytic reaction. The method of development of these rate equations has general similarities with the usual type of kinetic equations, such as those of Hougen and Watson,[68] except that the equations for the amounts of gas adsorbed and the rates of adsorption and desorption are not of the simple Langmuir type. Brunauer, Love, and Keenan [90] have derived equations for the adsorption isotherm and the

[89] P. H. Emmett and J. T. Kummer, *Ind. Eng. Chem.*, **35**, 677 (1943).

[90] S. Brunauer, K. S. Love, and R. G. Keenan, *J. Am. Chem. Soc.*, **64**, 751 (1942).

rates of adsorption and desorption by the general method of Langmuir, but with the assumption that the surface is heterogeneous; *ie*, the heats of adsorption and activation energies of adsorption are not constant but decrease linearly with the amount of gas adsorbed. These equations reduce to those of Temkin and Pyzhev for a limited range of coverage of the surface. From their general equations, Brunauer, Love, and Keenan [90] were able to calculate the adsorption isotherm of nitrogen at 396°C on a doubly promoted catalyst, as well as the rate equation for decomposition of ammonia, from data for the rate of adsorption of nitrogen.

The Catalytic Synthesis of Methanol and Higher Alcohols

The equilibrium constants for the synthesis of methanol from hydrogen and carbon monoxide are considerably less than one for temperatures at which the reaction is appreciably fast (temperatures greater than 300°C) as shown by data in Table 7 (Chapter 1, p 21). As in the ammonia synthesis, it is necessary to use moderately high pressures to realize appreciable yields of methanol. Thus, at 350°C and 100 and 300 atm of $2H_2$ to 1CO gas, the percentages of methanol at equilibrium are 3.7 and 19.5, respectively. The formation of higher alcohols is more favorable than that of methanol, and at the same pressure of operation the synthesis of higher alcohols is possible at considerably higher temperatures.

Methanol synthesis. Oxides of zinc, copper, chromium, manganese, uranium, beryllium, and zirconium are active in the synthesis, and some mixtures of these oxides show considerably greater activity than pure oxides. Cobalt, nickel, iron, platinum, and palladium catalyze reactions forming methane and free carbon under the conditions of operation. The alkaline earth metal oxides as well as those of magnesium, titanium, thorium, aluminum, silicon, molybdenum, vanadium, and tungsten are inactive.

Many of the papers on the methanol synthesis discuss the effect of catalyst composition on activity and product distribution. The decomposition of methanol at atmospheric pressure has been used by some workers as a simple method of assaying catalysts, and in some cases very good correlation between the activity for the synthesis and decomposition of methanol has been found. In the next few pages a detailed account of the activity of ZnO-CuO catalysts as a function of composition is presented.

Frolich, Fenske, and Quiggle [91] studied the decomposition of methanol on ZnO-CuO catalysts, as a function of catalyst composition. The ex-

[91] K. Frolich, M. R. Fenske, and D. Quiggle, *Ind. Eng. Chem.*, **20**, 694 (1928).

tent of decomposition of methanol at 360°C is shown in Figure 20, and the products formed per mole of methanol decomposed in Figure 21. Methanol decomposition was postulated to occur according to $CH_3OH \rightarrow HCHO + H_2$ followed by $HCHO \rightarrow CO + H_2$ and $HCHO \rightarrow \frac{1}{2}HCO_2CH_3$. Catalysts with less than 40 mole per cent of zinc oxide produced sizable amounts of methyl formate, whereas chiefly carbon monoxide was formed by catalysts with more than 50 mole per cent zinc oxide.

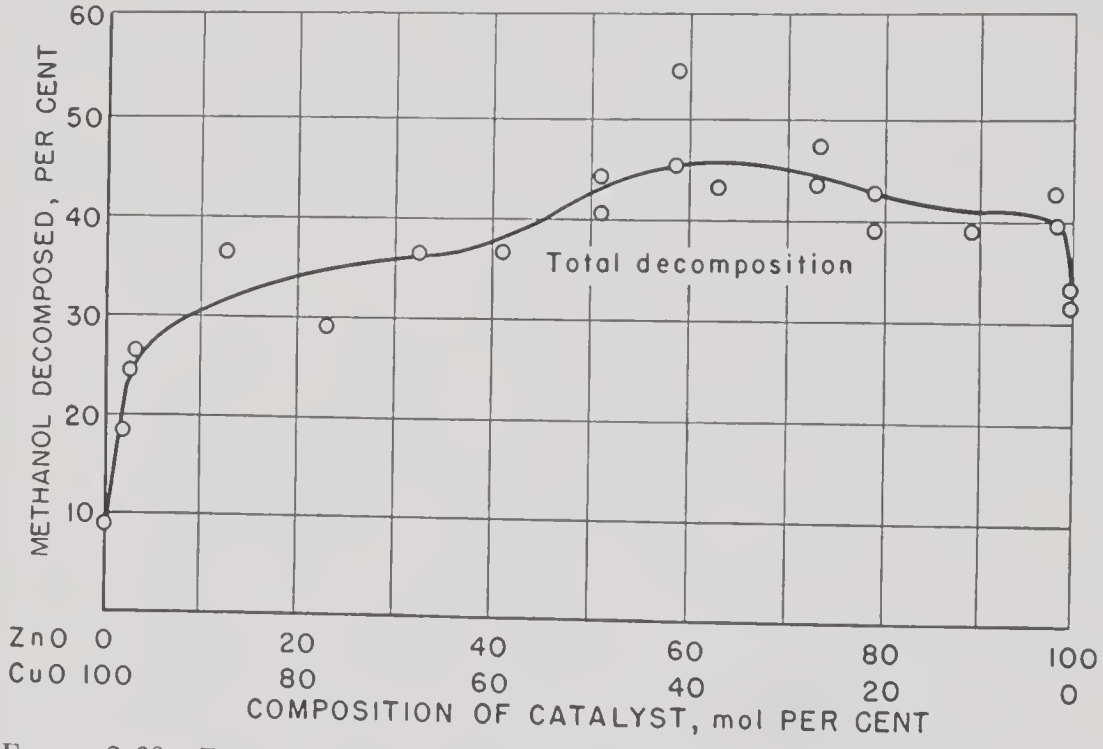


FIGURE 2–20. Decomposition of methanol at atmospheric pressure and 360°C as a function of composition of zinc oxide-copper oxide catalysts. Reproduced by permission from reference 92.

Formaldehyde was produced in small and nearly constant amounts with all these catalysts. The greatest activity for both total decomposition and decomposition to carbon monoxide was found between 60 and 70 mole per cent zinc oxide.

In the methanol synthesis [92] this series of catalysts also exhibited maximum activity at 60–70 mole per cent zinc oxide, as shown in Figure 22. Comparison between the rates of decomposition and synthesis is shown in Figure 23. The correlation between decomposition and synthesis activity is very good, if the decomposition to carbon monoxide is used in the comparison; however, the comparison between synthesis and total decomposition is very much less satisfactory. Studies of a

[92] P. K. Frolich, M. R. Fenske, P. S. Taylor, and C. A. Southwich, *ibid.*, **20**, 1,327 (1928).

catalyst by the reverse reaction are in some cases more simple experimentally than studies of the forward reaction; however, the results may not be very reliable. For example, Storch [93] found that the addition of

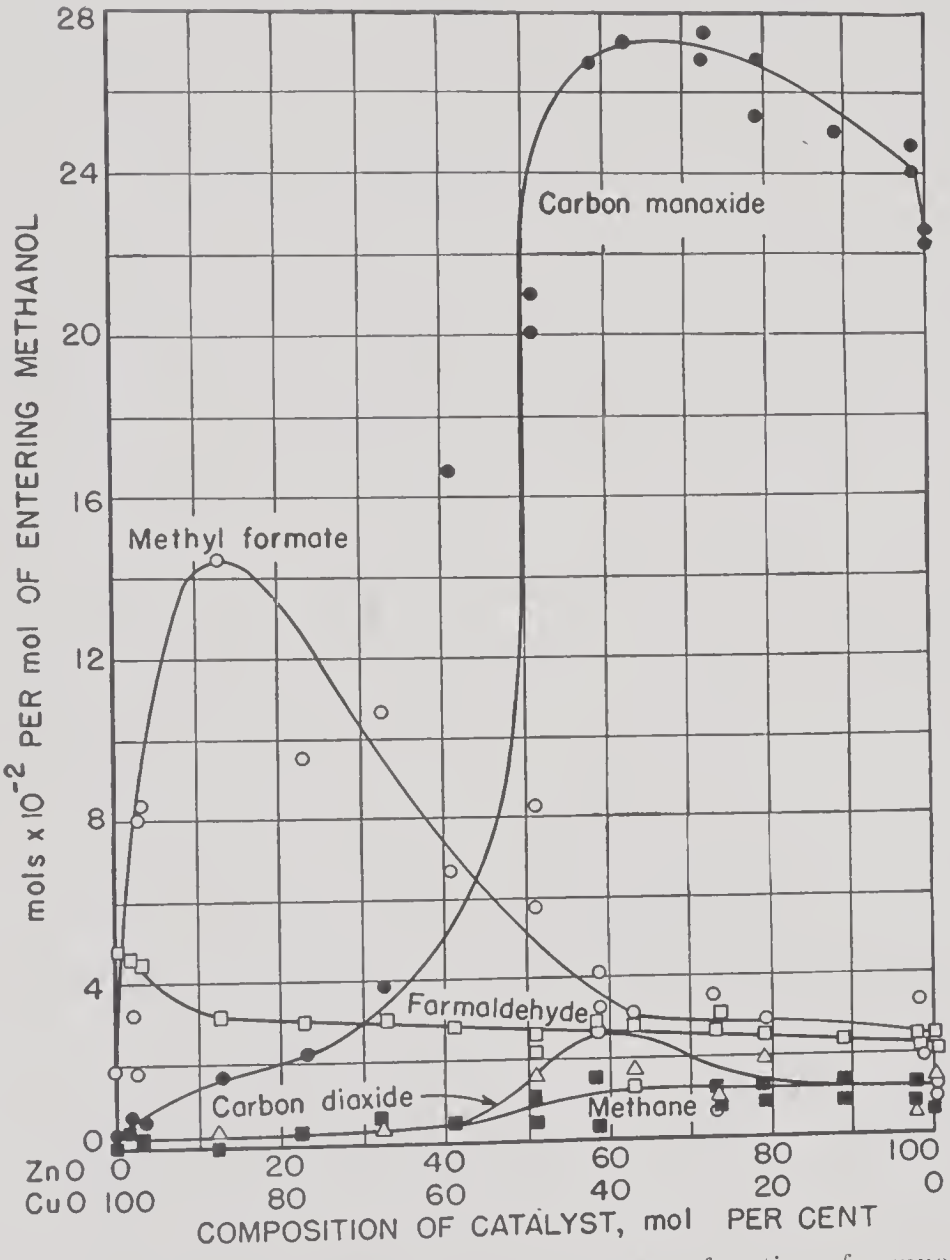


FIGURE 2-21. Products of methanol decomposition as a function of composition of copper oxide-zinc oxide catalysts at 360°C. Reproduced by permission from reference 91.

chromium oxide to a zinc oxide catalyst increased its activity in the methanol synthesis but did not change its catalytic activity in the decomposition of methanol.

The catalysts of Frolich were reduced in methanol vapor at 200°–220°C before use. The weight loss on reduction was usually greater

[93] H. H. Storch, *J. Phys. Chem.*, **32**, 1,743 (1928).

than that corresponding to complete reduction of the copper oxide, indicating some reduction of the zinc oxide (with the possible formation of α-brass). X-ray studies [94] of these catalysts showed that copper and zinc oxide have the same crystal structure as the pure materials, but have different lattice parameters in two-component catalysts. As shown in Figure 24, the lattice dimensions of copper increased with the amount of

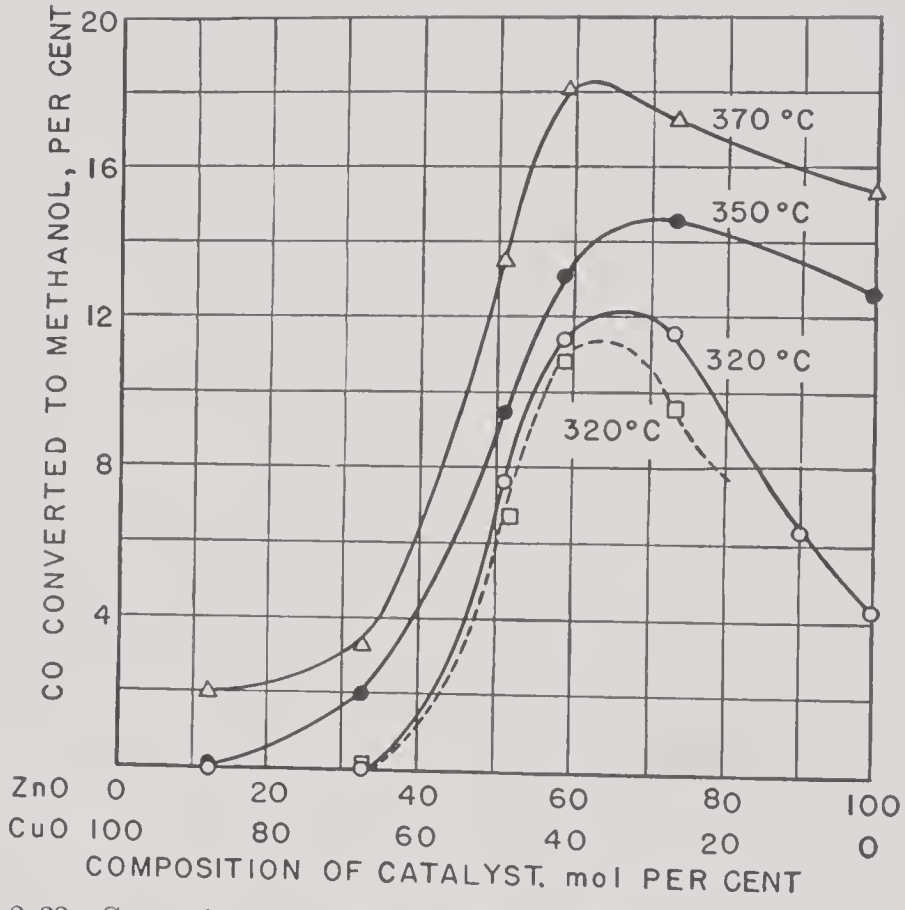


FIGURE 2–22. Conversion to methanol at 204 atm pressure and various temperatures as a function of composition of zinc oxide-copper oxide catalysts. Reproduced by permission from reference 92.

zinc oxide, passed through a maximum and a minimum, and finally increased again. With increase in copper content, the lattice parameter of zinc oxide decreased to a minimum and increased to a value greater than that of pure zinc oxide. The authors related the shorter dimension of the copper lattice to the decomposition of methanol to methyl formate as shown in Figure 25, and the shorter dimensions of the zinc oxide lattice to the activity for decomposition to carbon monoxide (Figure 26). The authors suggested that some of these effects may have been due to dif-

[94] P. K. Frolich, R. L. Davidson, and M. R. Fenske, *Ind. Eng. Chem.*, **21**, 109 (1929).

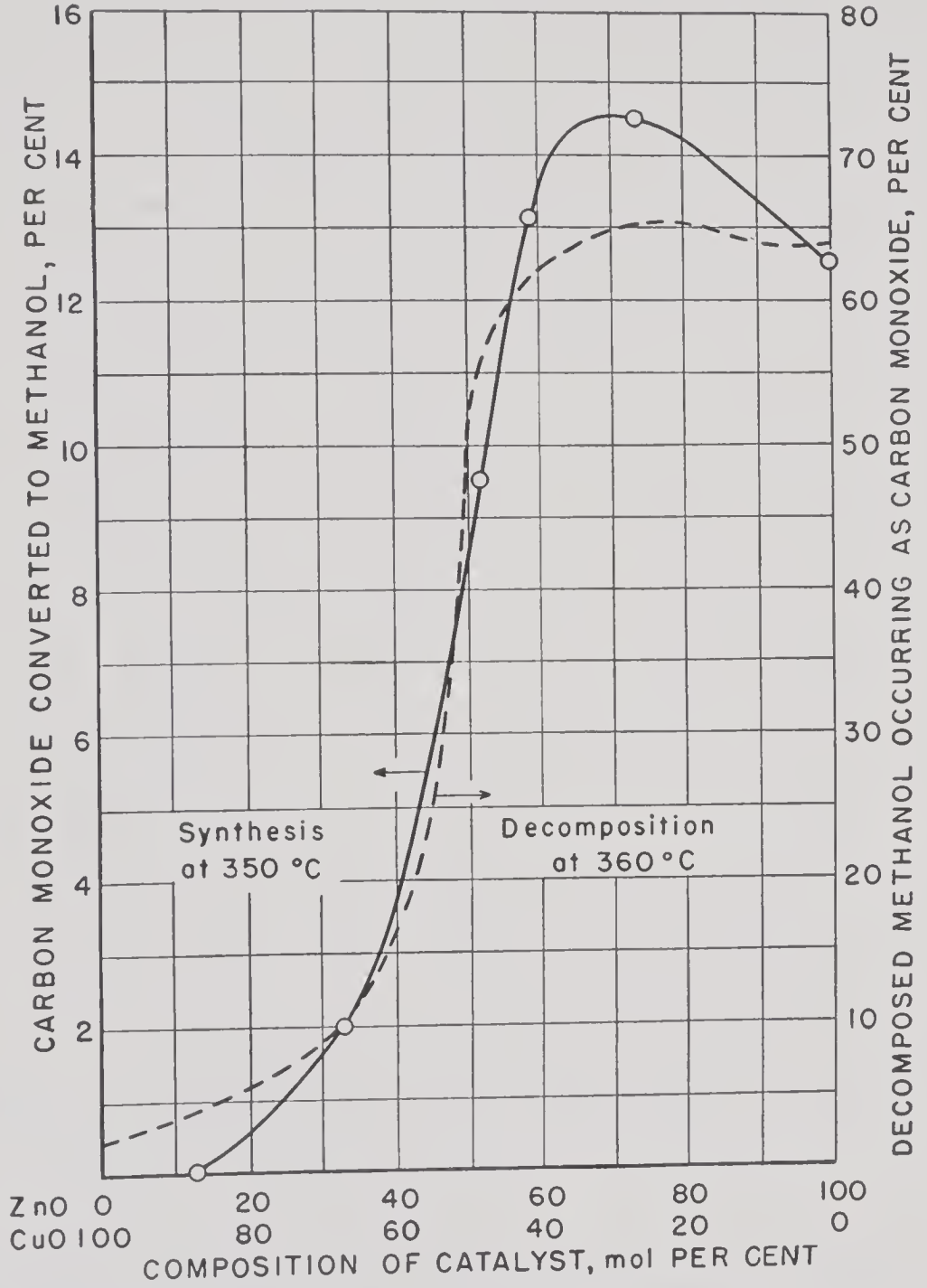


FIGURE 2–23. Comparison of methanol decomposition at atmospheric pressure and synthesis at 204 atm pressure with composition of zinc oxide-copper oxide catalysts. Reproduced by permission from reference 92.

ferences in surface area, but at that time no satisfactory method of area determination was available.

With ZnO-Cr_2O_3 gel catalysts, Frolich and Cryder [95] found maximum activity for the synthesis when the catalyst contained 75 mole per cent

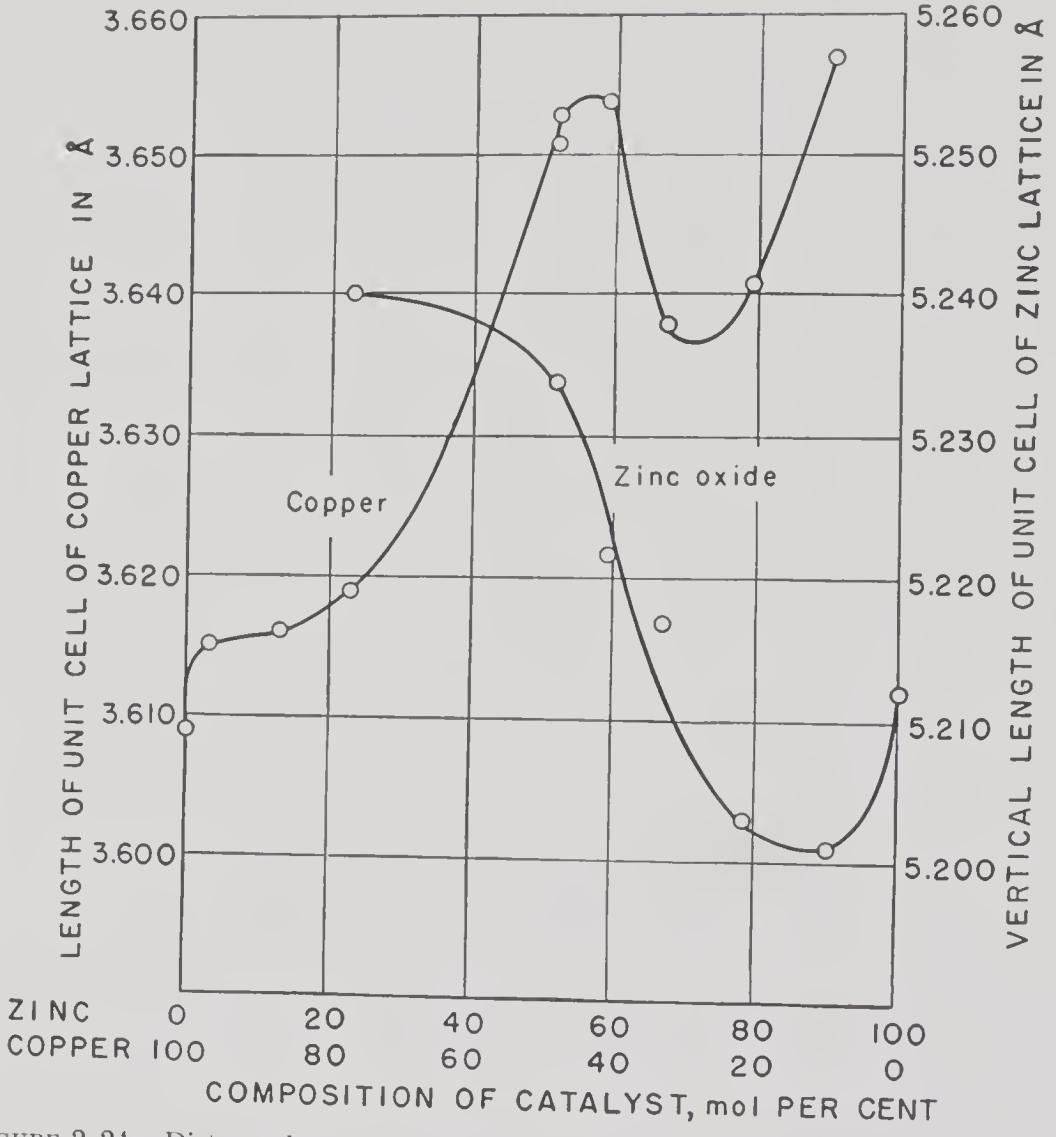


FIGURE 2-24. Distance between atoms in copper-zinc oxide catalysts as a function of catalyst composition. Reproduced by permission from reference 94.

Zn, and they observed satisfactory agreement between the activities for decomposition of methanol to carbon monoxide and for the synthesis, as shown in Figure 27. Fenske and Frolich [96] described a ternary catalyst of copper:zinc:chromium (49:43:8) that was very active in the synthesis.

[95] P. K. Frolich and D. S. Cryder, *ibid.*, **21**, 867 (1929).
[96] M. R. Fenske and P. K. Frolich, *ibid.*, **21**, 1,052 (1929).

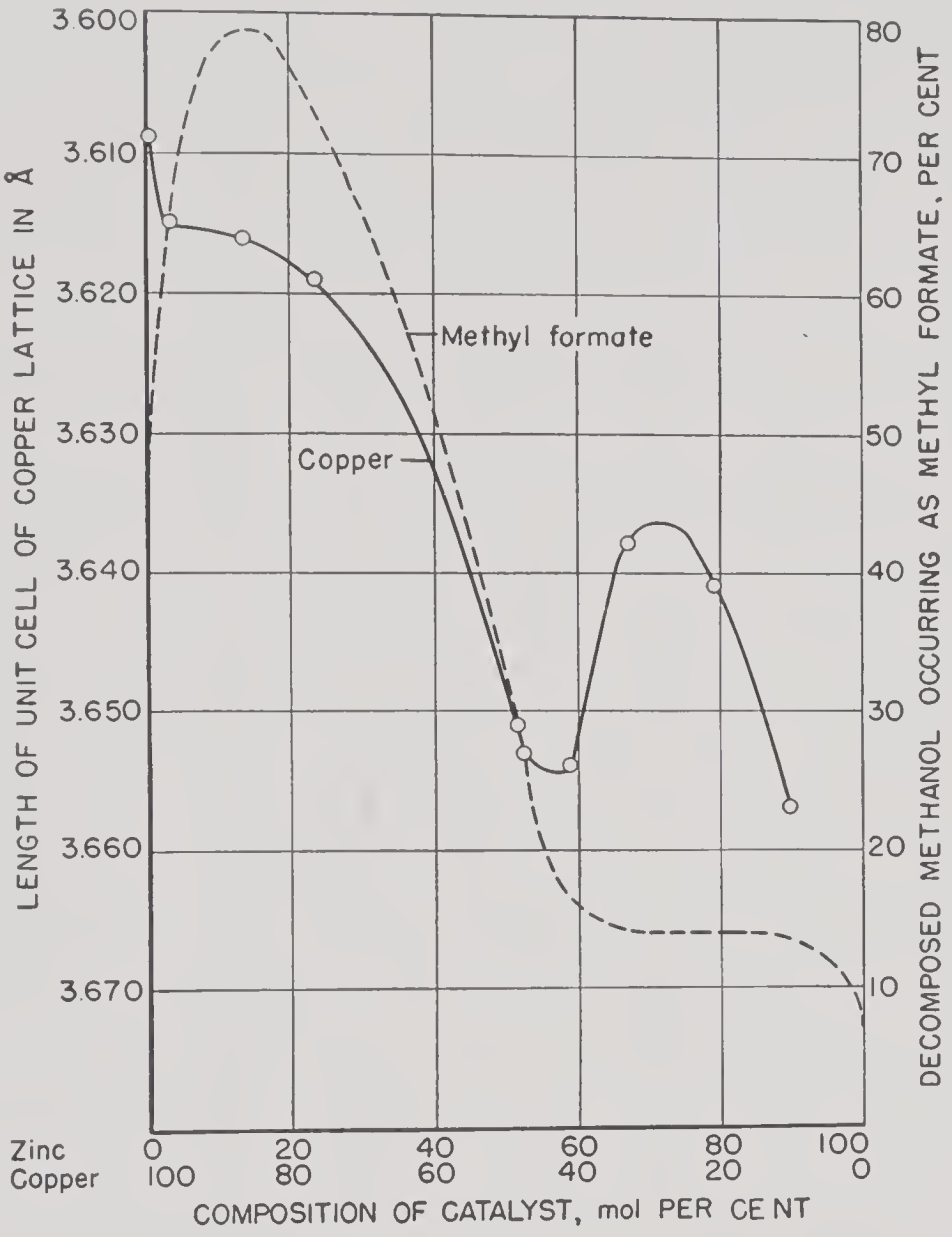


FIGURE 2–25. Comparison of the dimensions of the copper lattice with the decomposition of methanol to methyl formate as a function of composition of zinc oxide-copper oxide catalysts. Reproduced by permission from reference 94.

Dodge and Newton [97] considered the thermodynamics of the formation of formaldehyde and its hydrogenation to methanol according to reactions 47 and 48:

$$H_2 + CO = HCHO \qquad K_1 = \frac{p_{HCHO}}{p_{H_2} p_{CO}} \tag{47}$$

$$HCHO + H_2 = CH_3OH \qquad K_2 = \frac{p_{CH_3OH}}{p_{H_2} p_{HCHO}} \tag{48}$$

[97] B. F. Dodge and R. H. Newton, *J. Am. Chem. Soc.*, **55**, 4,747 (1933).

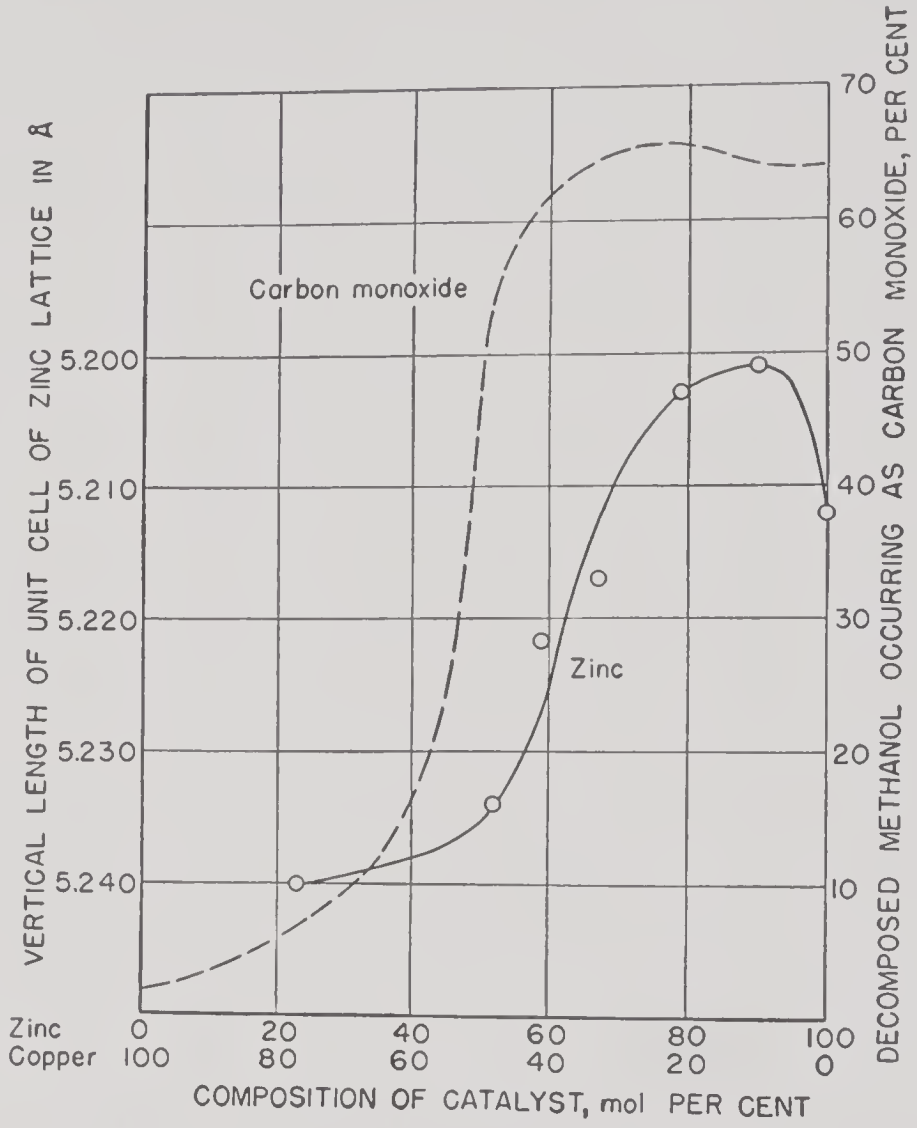


FIGURE 2–26. Comparison of the change in zinc oxide lattice with decomposition of methanol to carbon monoxide as a function of composition of zinc oxide-copper oxide catalyst. Reproduced by permission from reference 94.

and gave the values of K_1 as 1.9×10^{-5} and 1.5×10^{-5} and of K_2 as 210 and 8.3 at 250° and 350°C, respectively. Thus, formaldehyde, if formed as an intermediate, may be expected to be readily hydrogenated to methanol if the catalyst is suitable. Most workers suggest that formation of methanol proceeds through formaldehyde as an intermediate and all methanol catalysts are assumed to be effective in catalyzing reaction 48 so that little, if any, formaldehyde is found in the reaction products.

Brown and Galloway [98] found dimethyl ether in amounts as large as 10 per cent of the methanol from a normal zinc chromate catalyst. The

[98] R. L. Brown and A. E. Galloway, *Ind. Eng. Chem.*, **21**, 310 (1929).

ether formation was attributed to a subsequent dehydration of methanol on the catalyst, since the ratio of ether to alcohol decreased as the space velocity was increased.

Kinetic data for the methanol synthesis are meager. Lewis and Frolich [99] studied some of the variables of the synthesis on a precipitated

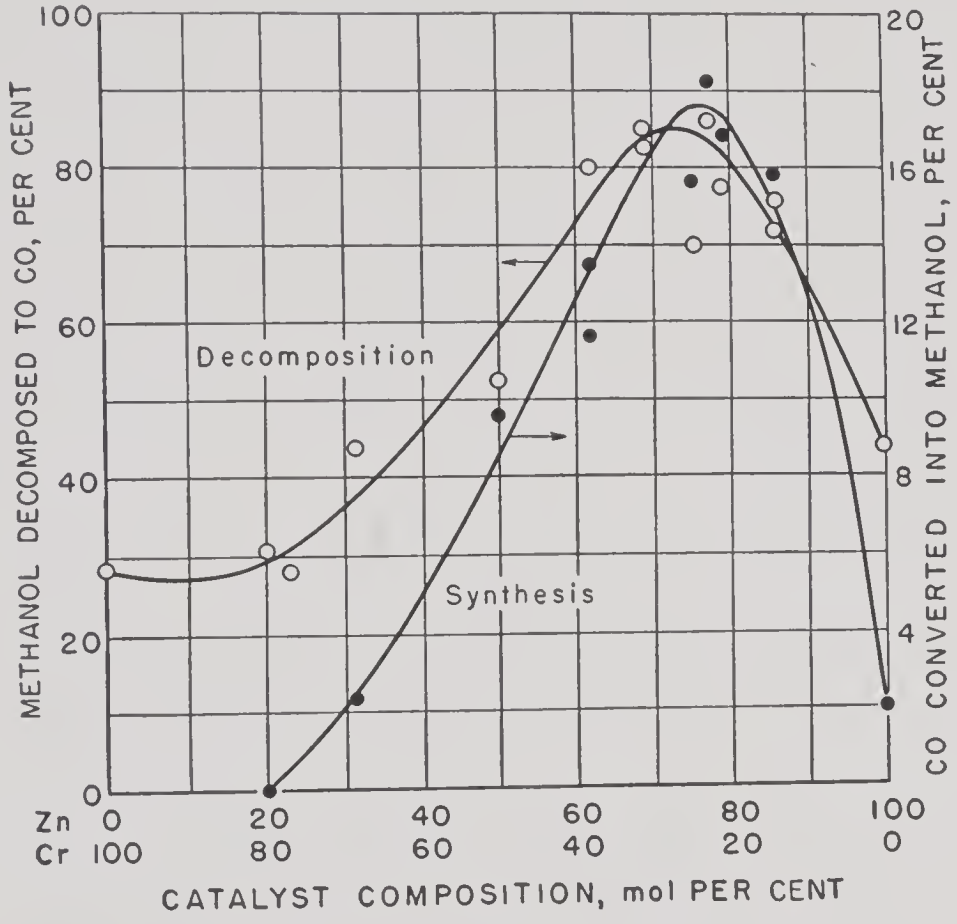


FIGURE 2–27. Comparison of methanol decomposition at 340°C and atmospheric pressure and synthesis at 350°C and 204 atm with composition of zinc oxide-chromium oxide catalysts. Reproduced by permission from reference 95.

zinc oxide-copper oxide-alumina-metallic copper supported catalyst ($ZnO:CuO:Al_2O_3:Cu$ support = 36:44:20:300) in a flowing high-pressure reactor. The gas was composed of 70 per cent hydrogen, 26 per cent carbon monoxide, and 4 per cent inerts. The space-time-yield at constant temperature increased with flow of gas, as shown in Figure 28, and increased with pressure, as shown in Figure 29. The fraction of the carbon monoxide converted to methanol at constant total pressure and flow increased with temperature to about 340°C and then decreased, as shown in Figure 30. This decrease was related to loss of catalytic

[99] W. K. Lewis and P. K. Frolich, *ibid.*, **20**, 285 (1928).

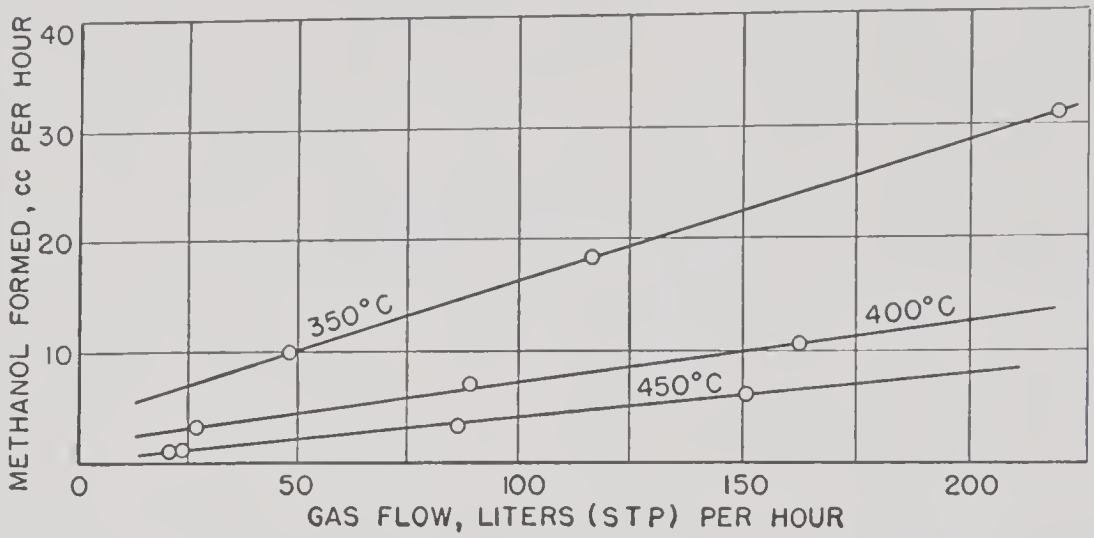


FIGURE 2–28. Space-time-yield of methanol as function of gas flow. 40 cc of zinc oxide-copper oxide-alumina catalyst tested at 204 atm pressure of $2.7H_2$ to 1CO gas. Reproduced by permission from reference 99.

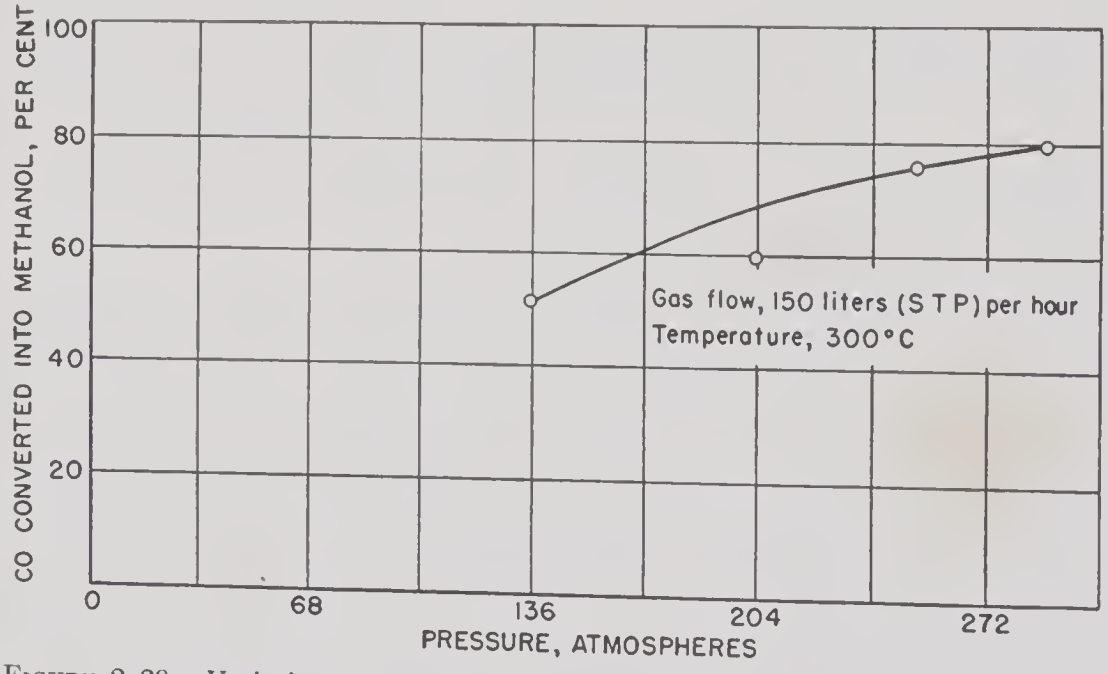


FIGURE 2–29. Variation of conversion to methanol with pressure. 40 cc of zinc oxide-copper oxide-alumina catalyst tested with $2.7H_2$ to 1CO gas. Reproduced by permission from reference 99.

activity at the higher temperatures, possibly because of sintering of the catalyst. At the higher temperatures, appreciable fractions of the carbon monoxide were converted to products other than methanol.

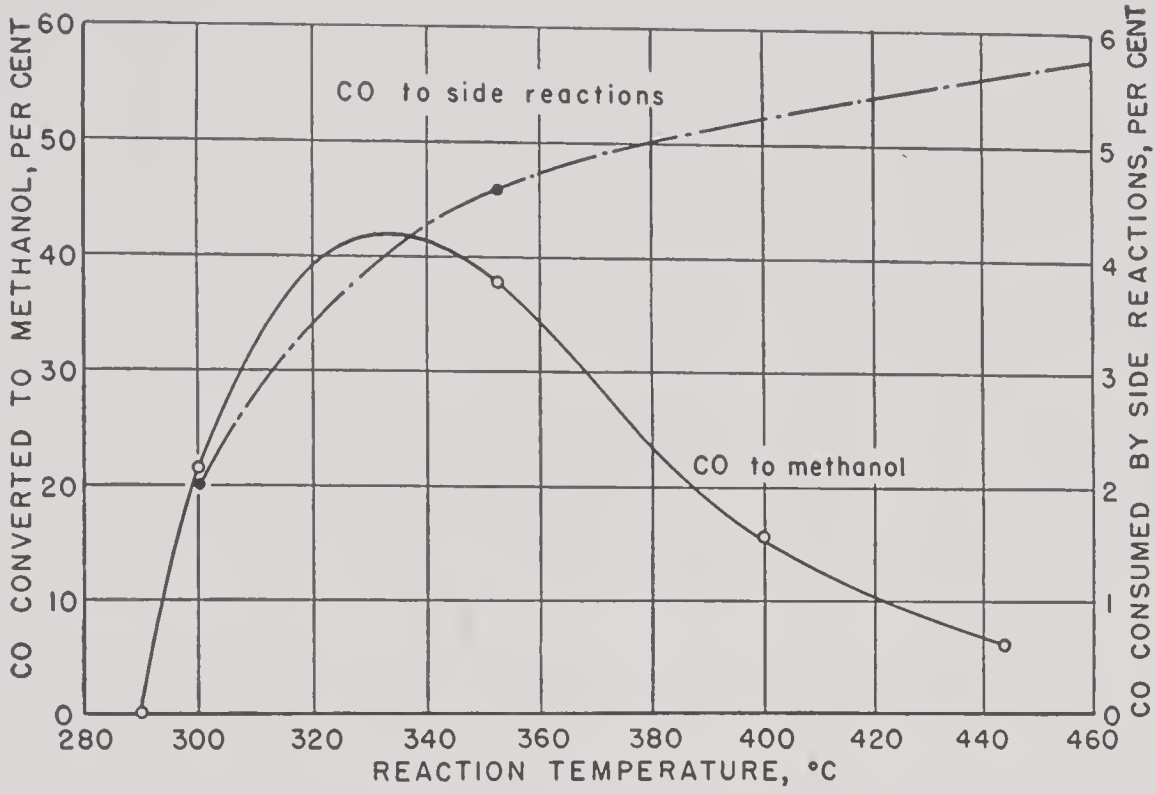


FIGURE 2–30. Effect of temperature on the methanol reaction on zinc oxide-copper oxide-alumina catalyst. 40 cc of catalyst at flow of 80 l (STP) per hr of $2.7H_2$ to 1CO gas at 204 atm pressure. Reproduced by permission from reference 99.

Synthesis of higher alcohols. The synthesis of higher alcohols is of special interest because of its similarity to the formation of higher hydrocarbons by the Fischer-Tropsch synthesis. The formation of higher alcohols is more favorable thermodynamically than that of methanol. Fischer [100] showed that alkalized iron catalysts formed mixtures of hydrocarbons and alcohols, both containing compounds of more than one carbon atom. At 460°–490°C and 240 atm, a zinc oxide-chromium oxide-potassium carbonate catalyst [101] produced liquid products containing 17.8 per cent methanol, 2.3 per cent ethanol, 33.4 per cent propanols, 2.5 per cent butanols, 9 per cent amyl alcohols, small amounts of higher alcohols, and 36 per cent water. Morgan [102] showed that the presence of alkali oxides (and CaO) increased the yield of higher alcohols from a Cr_2O_3-MnO catalyst.

[100] F. Fischer, *ibid.*, **17**, 574 (1925).

[101] P. K. Frolich and W. K. Lewis, *ibid.*, **20**, 354 (1928).

[102] G. T. Morgan, D. V. N. Douglas, and R. A. Proctor, *J. Soc. Chem. Ind. (London)*, **51**, 1T (1932).

The criteria for synthesis of higher alcohols may be summarized as follows:

1. Methanol catalyst plus alkali.

2. Higher temperatures than required for the methanol synthesis; 400°–500°C as compared with 325°–375°C for methanol synthesis. It

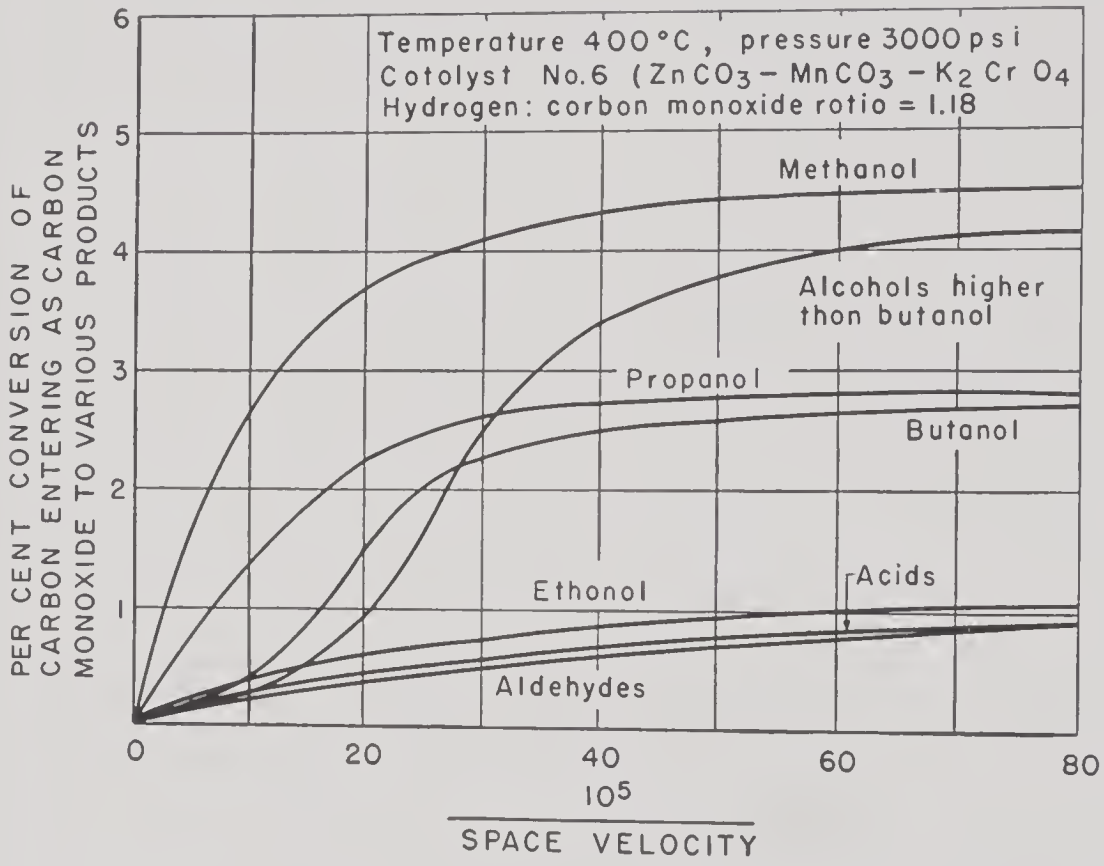


FIGURE 2–31. Conversion of carbon monoxide to higher alcohols as a function of the reciprocal of space velocity. Reproduced by permission from reference 103.

should be noted that the equilibrium concentration of methanol at 400°C and 300 atm with $2H_2 + 1CO$ gas is only 6.3 per cent.

3. Lower space velocities than those used in the methanol synthesis.[103]

Frolich and Cryder [103] studied the reaction mechanism of the higher alcohol synthesis on a ZnO-MnO-K_2CrO_4 catalyst. Figure 31 presents the product distribution as a function of space velocity. The yields of methanol were greater than those of any other alcohol at all space velocities, indicating that the products were not present in equilibrium amounts. At high flows, methanol was the chief product, but at lower flows the amounts of higher alcohols increased. The yield of ethanol was less than that of C_3 or C_4 alcohols. Only small amounts of acetic acid and ketones were formed, and most of the acids were present as

[103] P. K. Frolich and D. S. Cryder, *Ind. Eng. Chem.*, **22**, 1,051 (1930).

esters. These data indicate that methanol may be an intermediate in the synthesis and that the rate-controlling step may be the formation of ethanol, since its concentration is much lower than that of methanol or higher alcohols. The distribution of alcohols is strikingly similar to the products from Fischer-Tropsch synthesis, in which the yields of C_2 hydrocarbons are lower than methane, C_3, or C_4 hydrocarbons.

Frolich and Cryder [103] arranged experiments to test the hypothesis of Fischer for synthesis of higher alcohols. Fischer [100] postulated the following successive reactions:

$$CH_3OH + CO = CH_3COOH \tag{49}$$

$$CH_3COOH + H_2 = CH_3CHO + H_2O \tag{50}$$

$$CH_3CHO + H_2 = CH_3CH_2OH \tag{51}$$

and similar reactions with ethanol to form propanol, etc. For secondary alcohols, acetic acid was postulated to decompose to form acetone, which was hydrogenated to isopropyl alcohol according to

$$2CH_3COOH = (CH_3)_2CO + CO_2 + H_2O \tag{52}$$

$$(CH_3)_2CO + H_2 = (CH_3)_2CHOH \tag{53}$$

Frolich and Cryder [103] performed numerous experiments in which various alcohols, aldehydes, acids, and ethers together with hydrogen, carbon monoxide, or water were passed over a catalyst in a high-pressure flowing system. The formation of higher alcohols from methanol and hydrogen or carbon monoxide showed no striking differences in velocity or product distribution, and the authors believed that the formation of higher alcohols was not primarily dependent on either hydrogen or carbon monoxide. Water was found to inhibit the reaction forming higher alcohols, and the presence of excess carbon monoxide was advantageous since it removed the water by the water-gas reaction. A mixture of methanol, ethanol, and hydrogen produced mostly propanol.

The authors concluded that the mechanism of Fischer did not adequately explain their data and proposed a condensation mechanism such as

$$CH_3OH + CH_3OH = C_2H_5OH + H_2O \tag{54}$$

This type of reaction would be independent of hydrogen and carbon monoxide, except to the extent that carbon monoxide accelerates the reaction by removing water. Reaction of methanol and ethanol should yield propanol by this mechanism. By variations of this mechanism, secondary alcohols can be formed. It should be noted that there is some ambiguity in the "introduction of possible intermediate compounds"

method of studying mechanisms, because these compounds may decompose to extents approaching equilibrium concentration of hydrogen and carbon monoxide if the rate of decomposition is sufficiently high. Higher alcohols could possibly be formed from this hydrogen and carbon monoxide.

Graves [104] carefully fractionated the products of the commercial synthesis of higher alcohols and identified by preparation of derivatives a number of the higher alcohols as follows:

Primary Alcohols (48.5 per cent)	Secondary Alcohols (51.5 per cent)
n-Propanol	Isopropanol
Isobutanol	3-Methyl-2-butanol
2-Methyl-1-butanol	2,4-Dimethyl-3-pentanol
2-Methyl-1-pentanol	3-Pentanol [a]
2,4-Dimethyl-1-pentanol	2-Pentanol [a]
4-Methyl-1-hexanol	2-Methyl-3-pentanol [a]
2,4-Dimethyl-1-hexanol [a]	
4- or 5-Methyl-1-heptanol [a]	

[a] There is some uncertainty concerning these identifications because derivatives of these compounds had not been described in literature.

Tests for tertiary alcohols were negative. Traces of aldehydes, ketones, and saturated and unsaturated hydrocarbons were found. Not all the product was identified, but the author states that *n*-butanol was not found. The postulated mechanisms of Fischer [100] and Frolich [103] were considered with respect to the products found. The mechanism of Fischer for primary alcohols would result in only straight-chain alcohols and thus does not explain the observed products. The mechanism of Frolich involving the condensation of primary alcohols together with the following postulates explains the presence of all primary alcohols identified and the absence of others:

1. "Higher alcohols are formed by intermolecular dehydration of two lower alcohol molecules," such as reaction 54.

2. "Dehydration may involve a hydrogen atom on the carbon atom of methanol, but such reactions are slow, compared to one involving a hydrogen on a β-carbon atom."

3. "Condensation takes place with difficulty on a CH_3 group and does not take place on a CH group. Most of the higher alcohols result from a condensation on a CH_2 group."

The formation of secondary alcohols involves the condensation of a hydrogen atom from the carbon atom holding the hydroxyl group.

[104] G. D. Graves, *ibid.*, **23**, 1,381 (1931).

Thus, the reaction of methanol plus ethanol to form isopropanol is represented as

$$CH_3OH + \underset{\displaystyle CH_3}{\underset{|}{H}}CHOH = \underset{\displaystyle CH_3}{\underset{|}{CH}}OH + H_2O \qquad (55)$$

A quantitative but less detailed analysis of the product from the higher alcohol synthesis with an alkalized zinc oxide catalyst is found in captured German documents, as shown in Table 9.[105]

Table 9. Composition of Product from the Higher Alcohol Synthesis [a]

Compound or Distillation Cut	Per Cent
Dimethyl ether	3.0
Methanol	51.2
Methanol-ethanol	0.4
Propanol	1.5
Isobutyl alcohol	11.5
Isoamyl	1.1
Fraction, 145°–163°C	2.9
Fraction, 160°–200°C	1.0
Fraction, 200°–270°C	0.7
Fraction, above 270°C	0.2
Isobutyrone	0.8
Water and losses	24.2

Also very small amounts of propylene, di- and tri-isobutylene, and propylcyclohexane.

[a] Reference 105.

Criterion for Successful Catalysts and Reasons for Loss of Catalytic Activity

To conclude and summarize this chapter on heterogeneous catalysis we shall discuss factors related to catalytic activity and to the decrease in activity. These factors vary considerably with individual reactions and catalysts, and only generalizations can be made. The catalyst must have sufficient mechanical strength and stability for use in the process; these requirements of the catalyst will vary considerably with the type of reactor in which the catalyst is used. For most reactions a moderately large and reasonably accessible surface is required, and, in general, catalysts with surface areas considerably smaller than 1 sq m per g may not prove suitable. Structural promoters and supports may provide and

[105] Harnisch, I.G. Leuna, T.O.M. Reel 134, Section V, Item 2.

maintain suitable mechanical strength and stability, surface area, and pore structure.

Suitable mechanical properties and pore geometry are necessary but not sufficient requirements for catalysis. The chemical nature of the surface determines whether a reaction occurs at all, and, if it does, what the course of the reaction will be. Catalytic reactions are usually specific, and in many cases the products formed are not those most stable thermodynamically. The course of a reaction depends upon chemical interactions between the catalyst and reactants and probably upon the spacing of catalyst atoms as well as specific effects of these atoms. Most studies indicate that surfaces of catalysts are heterogeneous; that is, certain portions of the surface have greater intrinsic activity than others and may even catalyze different reactions. This greater activity has been attributed to atoms at corners and edges of crystal lattices with relatively unsaturated valence forces and to atoms in incomplete or distorted crystal lattices, but some of the effects attributed to heterogeneity may be due to the accessibility of different parts of the surface. Promoters and, in some cases, supports may inhibit formation of a stable, ordered crystal structure.

Certain promoters that have no apparent effect on the catalyst structure may change the course of the reaction to a considerable extent or greatly increase its rate. Thus, by selection of suitable active components and promoters, desired reactions may be accelerated and undesirable ones may be inhibited or even prevented entirely.

In most catalytic reactions, there is little knowledge of the nature of the surface atoms and the chemically and physically adsorbed reactants and products at the surface. The surface atoms usually have considerably different thermodynamic properties from those of the bulk material, and in most cases surface complexes are difficult to study experimentally. With the possible exception of two or three catalysts the question "What is the active catalytic substance and its environment?" cannot be answered with any degree of exactness.

The life of catalysts varies considerably, depending upon the nature of the catalyst and reaction in which it is employed. The causes of catalyst failure may be divided into three groups: (1) failure of mechanical properties, (2) poisoning, and (3) sintering. Mechanical failure may result from attrition, crumbling of the catalyst particles due to changes in crystal structure, or deposition of material within the catalyst, causing rupture or swelling of the particles. This may result in plugging of fixed-bed reactors or marked changes in "fluid" properties of catalysts suspended in streams of gases or liquids. Another type of mechanical failure is the removal of catalytic materials by volatilization or solution,

which results in either loss of activity or change in the course of the reaction. The method of preparation and the selection of suitable active components, promoters, and supports can retard or prevent processes leading to mechanical failure. The rate of reactions causing catalyst disintegration usually increases with temperature; therefore overheating by ineffective heat transfer or improper operating conditions may cause mechanical failure and loss of activity.

Loss of catalytic activity may result from poisoning by traces of impurities in the reactants or by products formed in the reaction. The poisons may be adsorbed tenaciously on the active portions of the catalyst or may merely accumulate at the surface, causing portions of the catalyst to become inaccessible. Some poisons may be easily removed by solvent treatment, hydrogenation, or oxidation so that the catalyst is restored to nearly its initial activity. Other poisons cannot be removed by methods that do not in themselves destroy the catalytic activity. Sometimes it is possible to make the catalyst more resistant to poisoning by adding promoters or by varying the pore structure.

Sintering is an irreversible process involving the formation of more stable crystal structures or lower surface areas, and in sintering it is probable that the activity per unit surface area as well as the magnitude of the surface decreases. In some cases the presence of structural promoters decreases sintering to a negligible rate. The rate of sintering increases rapidly with temperature; hence, overheating or operation of the catalyst at too high a temperature may cause inactivation.

In the past thirty years, the knowledge of catalysis has increased greatly, chiefly through the development and judicious use of techniques for determining the chemical and physical nature of catalysts such as described in this chapter. We may ask about the extent to which the activity, selectivity, and durability of catalysts may be predicted from these properties of catalysts. In most cases the answer is that actual testing is the only reliable method of assaying catalysts for activity, selectivity, and life. These quantities are usually very complicated functions of the chemical (chemical composition including traces of impurities, phases present, lattice spacings, etc) and physical (extent and accessibility of surface, size of crystallites, etc) nature of the catalyst. In general, for a series of catalysts that differ widely in composition and method of preparation, the number of variables affecting performance is too great to permit a simple correlation with any one of the properties, such as surface area or the amount of a given phase. For catalysts of similar composition and method of preparation, a correlation of catalyst performance with properties of the catalyst may show a strong dependence of performance on one or more of the properties. After such a

relationship has been established, the activity or selectivity may be estimated with some degree of certainty from one or more of the properties. Most catalytic systems are of such complexity that the only rational approach to catalyst development requires consideration of all available information on the chemical and physical nature of the catalyst with respect to its performance in the catalytic reaction.

Studies of the kinetics of catalytic reactions are of great importance since they provide: (*a*) data required for design of reactors and auxiliary equipment, and (*b*) information as to the mechanism of the catalytic reaction. For rational design of reactors, the necessity for precise data on the dependency of rate and selectivity on operating variables, such as total pressure, partial pressures of reactants and products, space velocity, and temperature, is generally accepted. From kinetic studies valuable information about the mechanism of the catalytic reaction may be obtained. Determining the mechanism of catalytic reactions is a difficult task, even in very simple reactions, and it requires consideration of all available data on the kinetics and selectivity of the process as well as information about the chemical and physical properties of the catalysts. Once the reaction mechanism is established, catalyst and process development can proceed in a rational rather than an empirical or semi-empirical manner.

CHAPTER

3

In the Fischer-Tropsch synthesis, carbon monoxide is hydrogenated in the presence of a catalyst of which the chief constituent is nickel, cobalt, iron, or ruthenium. The optimum temperature ranges are 170°–205°C for nickel and cobalt, 200°–325°C for iron, and 160°–225°C for ruthenium. Nickel catalysts are best operated at atmospheric pressure, cobalt and iron up to about 20 atm, and ruthenium at 100 atm. The products obtained from the synthesis consist chiefly of straight-chain paraffin hydrocarbons. Secondary products include branched-chain hydrocarbons, aliphatic alcohols, aldehydes, and acids. The distribution of these products varies considerably and is dependent upon the catalyst and the synthesis conditions, as will be shown in this and the next chapter. This chapter is concerned with the development of Fischer-Tropsch catalysts, and Chapter 4 with the Fischer-Tropsch process development.

Discovery of Synthesis

In 1902, Sabatier and Senderens [1,2] observed that reduced nickel catalyzed the synthesis of methane from hydrogen-carbon monoxide ($3H_2 + 1CO$) or hydrogen-carbon dioxide ($4H_2 + 1CO_2$) mixtures at a temperature between 200° and 300°C. At temperatures of 270°–300°C methane was produced over a reduced cobalt catalyst. The Badische Anilin und Soda Fabrik [3] reported in 1913 that hydrogen and carbon monoxide reacted at 100–200 atm pressure and temperatures of 300°–400°C in the presence of alkali-activated cobalt and osmium oxides supported on asbestos to form a liquid product containing alcohols, aldehydes, ketones, fatty acids, and some saturated and unsaturated aliphatic hydrocarbons.

[1] P. Sabatier, *Die Katalyse*, Leipzig, 1927, pp 114, 144; P. Sabatier and J. B. Senderens, *Compt. rend.*, **134**, 514–6 (1902); *J. Soc. Chem. Ind.*, **21**, 504 (1902).

[2] P. Sabatier and E. E. Reid, *Catalysis in Organic Chemistry*, D. Van Nostrand Co., 1927, pp 179–80.

[3] Badische Anilin u. Soda Fabrik, German Patents 293,787 (1913); 295,202 (1914); 295,203 (1914).

This work led eventually to the development of the methanol synthesis by the same company.

After several years of experimental work in the Fuel Research Laboratories of the Kaiser Wilhelm Institut für Kohlenforschung, Mülheim-Ruhr, Germany, Franz Fischer and Hans Tropsch [4] in 1923 disclosed that alkalized iron turnings catalyzed the production of an oily liquid from hydrogen and carbon monoxide when the reaction was carried out in a tubular, electrically heated high-pressure reactor at 100–150 atm and 400°–450°C. This product, which was called "synthol," contained chiefly oxygenated compounds, such as alcohols, acids, aldehydes, ketones, and esters, and a very small quantity of hydrocarbons. Since the objective of German research at this time was the production of substitutes for natural gasoline and motor fuel, the investigation was directed towards increasing the hydrocarbon and decreasing the oxygenated fractions. Fischer and Tropsch found that the synthol catalyst at lower pressures of about 7 atm produced a mixture consisting chiefly of olefinic and paraffinic hydrocarbons and containing only a small fraction of oxygenated organic compounds. They observed also that methanization catalysts produced not only methane but its homologs at atmospheric pressure and low temperatures. However, at low pressures and temperatures, the activity decreased sharply and the yield of oil was very small. Consequently, more active catalysts were sought.

Early Catalysts Tests, 1925–1930

The first catalysts tested by Fischer were prepared by mixing the metal oxides or by decomposing mixtures of the dissolved or melted metal nitrates. The latter procedure appeared to be somewhat more efficient. The oxides were then reduced with pure hydrogen at about 350°C. At first, the oxides were used in the form of fine powders, which were difficult to handle. For this reason, the oxide mixture was sometimes pressed into a cake and broken into granules, sometimes compressed under pressure with a binder such as starch, and sometimes deposited on a carrier such as ceramic pieces, asbestos, clay chips, pumice stone, or activated charcoal. It was thought that the carrier might also help to preserve the surface of the catalyst. However, this was not so, for iron deposited on asbestos, for example.

The experiments of Fischer were carried out at atmospheric pressure in combustion tubes made of hard glass placed in a gas-heated, horizontal

[4] F. Fischer and H. Tropsch, *Brennstoff-Chem.*, **4**, 276–85 (1923); **5**, 201–8 (1924); **5**, 217–27 (1924).

aluminum-block furnace (Figure 1).[5,6] The oven consisted of a thick-walled cylindrical aluminum block of 80-mm O.D., 24-mm I.D., and 500-mm length. An opening 8 mm in diameter through the entire length of the block provided space for the temperature-measuring device. The block was completely insulated by diatomite stone. The furnace was heated by a series of burners and the temperature was kept automatically constant at ±1°C by a gas throttling device which was independent of variations in atmospheric pressure and room temperature. Narrow glass catalyst tubes, 4–5 mm I.D., were used, so that four catalysts could be

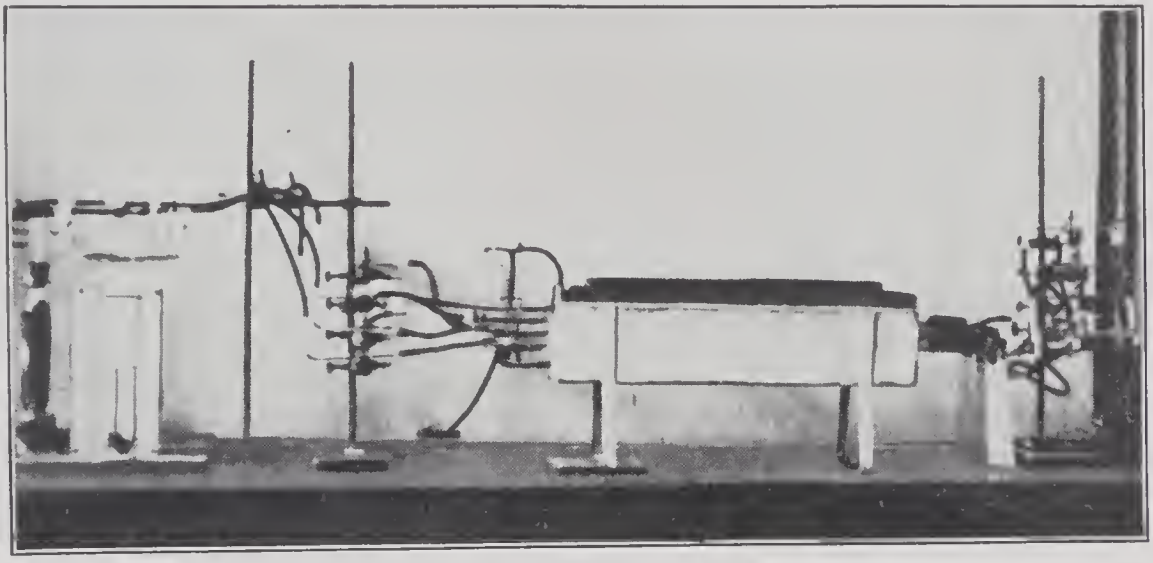


FIGURE 3-1. Early laboratory apparatus in Kaiser Wilhelm Institut. Reproduced from reference 5.

tested simultaneously in the furnace. Some tests were also made in catalyst tubes other than glass, such as iron, copper, and aluminum.

The mixture of carbon monoxide and hydrogen originating from a central laboratory circuit was passed through a wash bottle which was filled with water and which served as a bubble counter to regulate the flow of synthesis gas, then through a charcoal scrubber, and an in-gas flow meter. A three-way stopcock in front of the entrance to the catalyst tube permitted the gas to pass through the reactor or through a by-pass. By measuring the gas issuing from the catalyst tube and then the gas from the by-pass, the contraction in gas volume could be calculated. On the exit side of the catalyst tube, a trap collected product liquid at room temperature and a second three-way stopcock combined the two gas streams. The exit gas was measured by passage through a gasometer and then was led into a gas burette.

[5] F. Fischer and H. Tropsch, *Ges. Abhandl. Kenntnis Kohle*, **10**, 333–501 (1930).
[6] F. Fischer, *Brennstoff-Chem.*, **11**, 489–500 (1930); *Ges. Abhandl. Kenntnis Kohle*, **10**, 501–34 (1930).

At first, the composition of the product gases was determined by a gas analysis procedure in which the hydrocarbon mixture was burned with oxygen and the average molecular weight of the hydrocarbons estimated. More precise results were later obtained by a low-temperature distillation, in which the product gas was scrubbed free from carbon dioxide and moisture in soda-lime and calcium chloride traps and then led into an evacuated receiver cooled by liquid air. Carbon dioxide content was determined on another sample. Non-condensable gas was collected in a gasholder. The condensate was distilled *in vacuo*. Methane and other product gases thus obtained were added to the non-condensable gas in the gasholder; the whole quantity was measured and analyzed. The distillate was condensed in a second liquid-air-cooled receiver from which gasol (C_2, C_3, and C_4 hydrocarbons) was removed by distillation at $-90°C$ and analyzed. The saturated and unsaturated gaseous hydrocarbons were determined together by combustion with oxygen over platinized asbestos. The gasoline fraction (C_5+) was vaporized, mixed with nitrogen, and determined in the gas analysis apparatus; sometimes it was condensed in a small U-tube provided with two stopcocks and weighed.

In 1928, this condensation analysis procedure was replaced by direct determination of low-boiling hydrocarbons. The product gases were adsorbed on activated charcoal, from which the hydrocarbon products were stripped by heating and were condensed in an evacuated, liquid-air-cooled receiver. The receiver was then brought to room temperature and the volume or weight of gasoline measured directly.

The first catalyst that produced higher hydrocarbons in a systematic laboratory investigation at atmospheric pressure was reported by Fischer [7,8] in 1925. This catalyst was prepared by reduction at 400°C of a mixture of equal parts by weight of commercial iron oxide (obtained from the oxalate) and zinc oxide. The product gas obtained when 0.3 l per hour of $3H_2 + 1CO$ gas mixture was passed at 370°C over a layer of this catalyst 30 cm long contained 10 per cent by volume of hydrocarbons whose average carbon number was 1.2. Later tests were made with this catalyst at 270°C. Somewhat more active was a mixture of cobalt and chromic oxides, which at 270°C produced not only gaseous homologs of methane but also liquids and solids. When water gas was recycled over a catalyst obtained by reduction of a mixture of iron and cobalt oxides, yields up to 100 g of easily liquefiable (gasol), liquid, and solid hydro-

[7] F. Fischer and H. Tropsch, German Patent 484,337 (1925); *Brennstoff-Chem.*, **7**, 97–104 (1926); *Ber.*, **59**, 830–6, 923–5 (1926).

[8] F. Fischer, *Proc. Intern. Conf. Bituminous Coal, 1st Conf.*, 234–46 (1926).

carbons were produced, per cu m of water gas. Secondary products were water and carbon dioxide.

In 1926, Fischer [5] reported the results of exploratory studies at atmospheric pressure with metals of the eighth periodic group—the methanization catalysts. Finely divided iron, obtained by the hydrogen reduction of commercial iron oxide at 350°–500°C and retaining some residual oxide, produced a very small yield of gaseous higher hydrocarbons from a mixture of $2H_2 + 1CO$ gas at temperatures between 305° and 340°C. The chief secondary product was CO_2. When water gas was passed at 270°C over pure iron oxide prepared by decomposition of the nitrate, a contraction in gas volume of about 20 per cent was observed. Analysis of the products at the end of 50 hr gave the following composition, in grams per cubic meter of water gas at standard conditions: 1.9 methane, 37.3 C_1–C_4 hydrocarbons, and 11.6 C_5+. Iron combined with cobalt in the ratio of 1:1 produced a contraction in the volume of water gas of 50 per cent at 260°C and gaseous hydrocarbons whose average carbon number was 1.6. Iron-nickel in the atomic ratio of 1:1 and iron-cobalt-nickel in the ratio of 2:1:1 produced virtually no liquid hydrocarbons.

Finely divided cobalt was more effective than iron, in that it produced liquid hydrocarbon yields at a temperature 20° lower. A catalyst prepared by reducing pure cobalt oxide (from the nitrate) with water gas at 240°C and tested at 250°C produced after 90 hr a product of the following composition, in grams per cubic meter of water gas: 30.5 methane, 47.6 C_1–C_4 hydrocarbons, 10.5 C_5 and higher hydrocarbons, and 21 water. Nickel in a finely divided state showed virtually no activity as a catalyst for the synthesis of higher hydrocarbons.

Fischer soon recognized that reduction with hydrogen at temperatures higher than 350°C caused extensive decrease in catalyst surface, as a result of sintering, and produced catalysts of low activity. Tests were made with iron, cobalt, and nickel combined with difficulty reducible oxides, in the hope that sintering of the active metal constituent would be retarded.[5] The idea for using such combinations was based on the results observed with the first active catalyst, iron-zinc oxide. However, catalysts prepared by ignition of mixtures of the nitrates of iron and aluminum, lead, bismuth, or chromium showed very slight or no activity for the synthesis of liquid hydrocarbons. U. S. Bureau of Mines workers Smith, Davis, and Reynolds [9] in 1928 tested a synthetic-ammonia catalyst, which had been prepared by the reduction of fused magnetite promoted with potassium and aluminum oxides. With 150 cc of this catalyst in an experiment at 300°C and atmospheric pressure, no oil

[9] D. F. Smith, J. D. Davis, and D. A. Reynolds, *Ind. Eng. Chem.*, **20**, 462–4 (1928).

condensate was obtained, nor was any odor of higher hydrocarbons detected. Exit gas contained about 0.5 per cent each of carbon dioxide and methane. A small amount of slightly acid, watery condensate was present. The tests were made in the apparatus shown in Figure 2.[9] Synthesis gas was made by passing steam at a uniform rate into activated charcoal in a silica tube heated to about 950°C and was purified by passage through soda lime and activated charcoal scrubbers. The gas

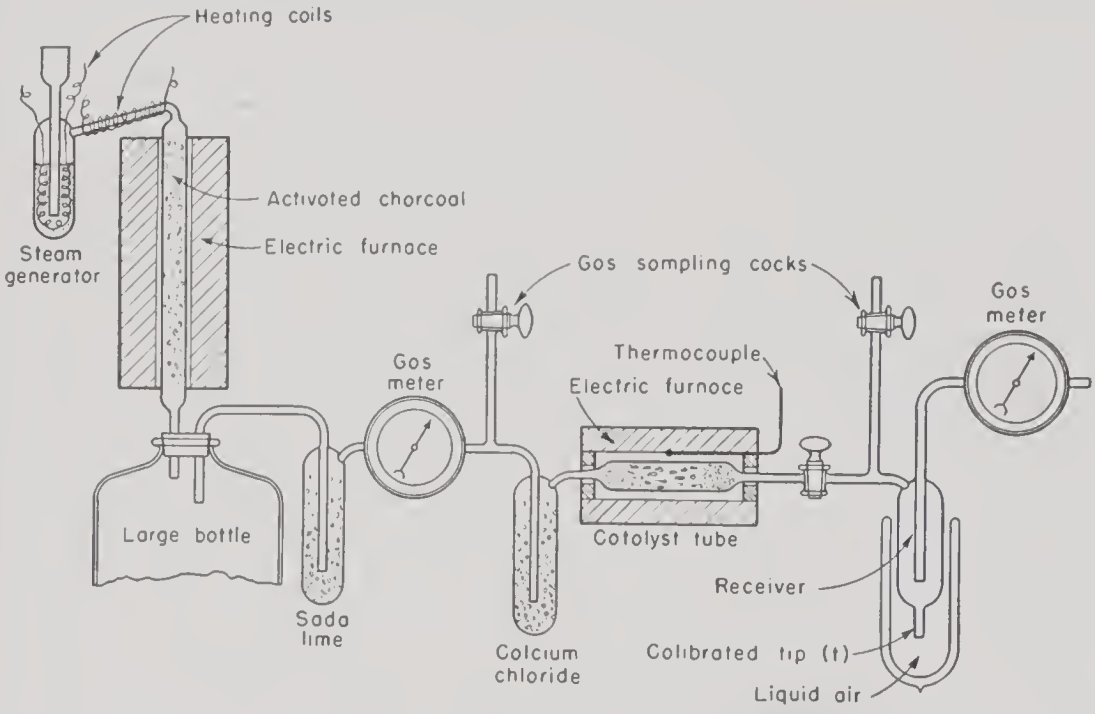


FIGURE 3–2. First U. S. Bureau of Mines laboratory apparatus for Fischer-Tropsch synthesis. Reproduced from reference 9.

mixture, consisting of equal volumes of pure carbon monoxide and hydrogen, was metered, dried, and passed into the catalyst tube. The exit gases were led into a receiver cooled in liquid air and provided at the bottom with a tip of small bore, and then through another gas meter. At the conclusion of an experiment, the receiver was allowed to warm up to room temperature, the escaping gas was collected for analysis, and the liquid products were collected in the tip. The volumes of water and of oily products were determined by measurement with a small cathetometer of the height of the column of liquid in the tip (*t*, Figure 2) which had been previously calibrated. Gas analyses of the incoming and exit gases were made at intervals. Temperatures were measured by means of a thermocouple attached to the outside wall of the catalyst tube at about the middle. The recorded temperatures represented the maximum temperatures at the exterior of the tube; the temperature at the ends of the furnace was somewhat lower.

In a modified catalyst-testing apparatus (Figure 3) [10] a fused-salt bath thermostatically controlled and heated electrically, to provide sensitive temperature control in the catalyst tube, was used. The testing apparatus to the right of (*e*) (except for the meters and gasholder) was made entirely of glass. Purified water gas was passed over the catalyst contained in the glass spiral (*h*), which was of small diameter in order to avoid overheating and was fitted with a loop (not shown in the figure) to preheat the entering gas to the temperature of the thermostat

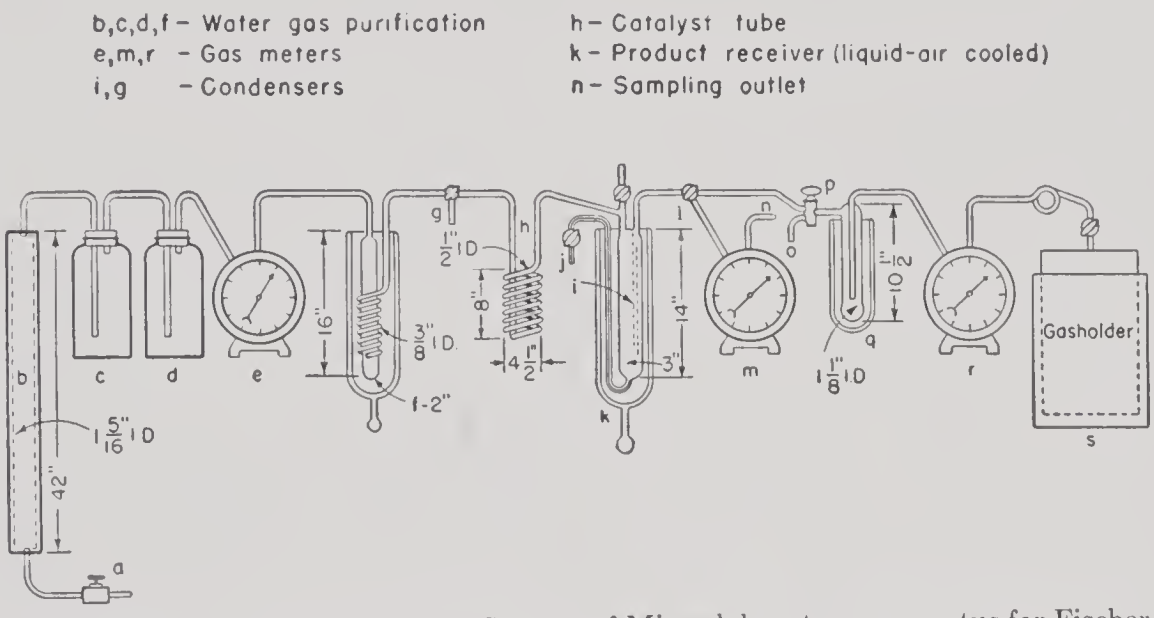


FIGURE 3–3. Early modified U. S. Bureau of Mines laboratory apparatus for Fischer-Tropsch synthesis. Reproduced from reference 10.

bath surrounding the catalyst tube. All products heavier than methane were collected in the receiver (*k*), cooled in liquid air. Also present at the conclusion of an experiment were occluded methane, carbon monoxide, and hydrogen; carbon dioxide; and water. Quantitative handling of these products was accomplished as follows: Condenser (*i*) was warmed to 0°C, the gaseous products passing through a fractionating condenser (*q*) cooled in carbon dioxide snow, which retained all hydrocarbons heavier than ethane and ethylene. The residual gas, freed from carbon dioxide by passage through a weighed potassium hydroxide solution, was measured (gas meter, *r*), and collected in the small gasholder (*s*). The hydrocarbons in (*q*) were distilled back into (*i*), which had again been cooled with liquid air, and were fractionally distilled by gradual warming up of the condenser.

Cobalt-vanadium oxide and cobalt-manganese oxide were inactive as catalysts.[5] In combination with rare earths, uranium oxide, and magnesium oxide, cobalt was only slightly active. Cobalt-chromium oxide

[10] D. F. Smith, C. O. Hawk, and D. A. Reynolds, *ibid.*, **20**, 1,341–8 (1928).

and cobalt-zinc oxide in ratios varying between 1:1 and 3:1 produced somewhat better yields of liquid hydrocarbons and water. Cobalt chromate, precipitated from a solution of cobaltous chloride with an excess of sodium chromate and reduced with hydrogen at 300°–350°C, was completely inactive when tested at atmospheric pressure.[9] Nickel combined with beryllium oxide produced a minute quantity of oil at a low temperature of 160°C.[5] However, all attempts before 1931 to obtain an active catalyst containing nickel were unsuccessful.

Because addition of difficultly reducible oxides and deposition of the catalyst oxides on certain carriers did not result in improved hydrocarbon productivity, the effect of copper oxide was studied.[5] Copper has a high heat conductivity and yet does not induce methane production. It was thought that the presence of copper would lower the temperature required for reduction of the catalyst oxides. Copper somewhat enhanced the activity of iron and cobalt, but not nickel. This was explained by Fischer on the basis of the tendency of nickel to form alloys with copper. Iron-copper catalysts are discussed in detail subsequently in this chapter (p 241). Cobalt-copper powder catalysts, containing the metals in the ratios 9:1 and 1:1, were tested at atmospheric pressure by Fischer.[5] The catalysts were prepared by decomposition of mixtures of the nitrates and were taken directly into synthesis at 220°C with water gas, without reduction by hydrogen. The cobalt-rich catalyst produced initially much methane and had a longer life. Cobalt-copper (9:1) deposited on Stüttgart carrier behaved much like the corresponding powdered catalyst; however, it lost activity more quickly because of smaller amount of catalyst material. Cobalt-copper (1:1) catalyst, precipitated by potassium hydroxide from a solution containing cobaltous chloride and cupric acetate and reduced with hydrogen at 300°–350°C, produced traces of oil on the watery condensate.[9] Cobalt-copper catalysts produced little oil; the oils obtained were always water-clear and colorless, in contrast to the oils from iron-copper catalysts, which were yellow. Cobalt catalysts produced more paraffin than iron catalysts, and water rather than carbon dioxide. A highly saturated product was obtained from a cobalt-copper catalyst tested at 190°C with $4H_2 + 1CO$ gas mixture.[11] The reaction water contained aldehydes and ketones, of which the chief component was acetone. Oil-soluble oxygenated compounds represented 6 per cent of the hydrocarbons boiling in the gasoline range and 2 per cent of the total hydrocarbon yield.

The effect of the addition of difficultly reduced metal oxides to act as

[11] F. Fischer and H. Tropsch, *Brennstoff-Chem.*, **9**, 21–4 (1928); H. Tropsch and H. Koch, *ibid.*, **10**, 337–46 (1929).

supports for the copper-containing catalysts was studied. Equally poor results were obtained with the oxides of beryllium, magnesium, zinc, cadmium, aluminum, tin, lead, chromium, and molybdic acid incorporated into the iron-copper catalyst.[5] Indeed, aluminum hydroxide appeared to deactivate the iron-copper catalyst. Fischer attributed this effect to the amphoteric character of aluminum hydroxide, which had an acidic effect under these conditions.

Cobalt-copper-magnesium oxide produced very little oil. Cobalt-copper (9:1) to which was added 10 per cent zinc oxide produced up to

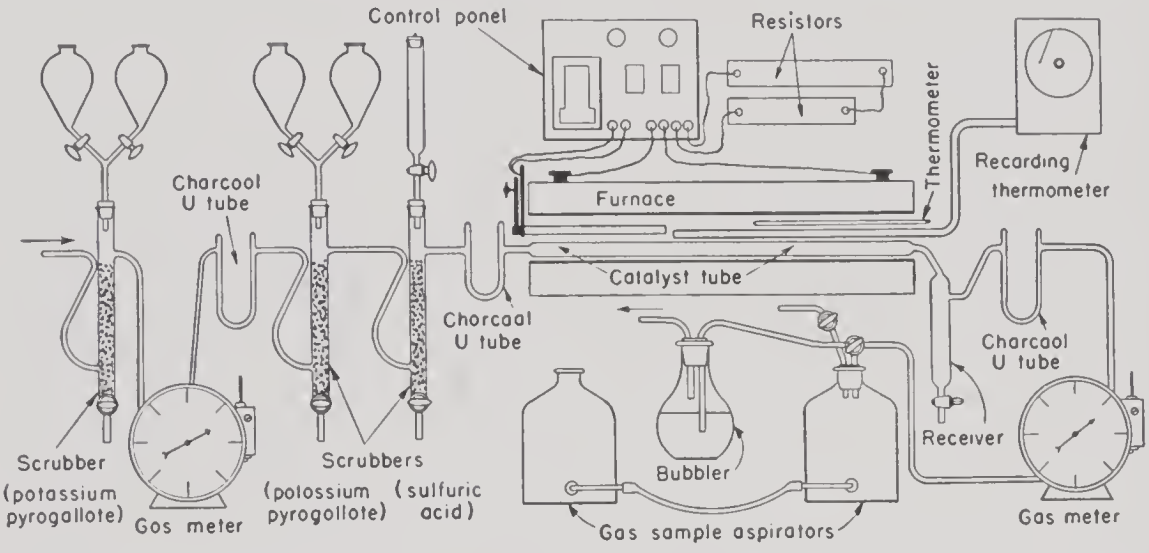


FIGURE 3–4. Early British catalyst-testing laboratory apparatus. Constructed from similar figure in reference 13*a*.

30 g of liquid hydrocarbons, per cu m of water gas, at 270°C. Erdely and Nash [12] reported very low yields of C_5+ hydrocarbons from cobalt-copper catalysts containing alumina, cerium oxide, and zinc oxide. The catalysts were tested in hard glass tubes placed horizontally in an electrically controlled furnace. The arrangement of the apparatus is shown in Figure 4.[13] After the catalysts were reduced in the electric furnace by the passage of hydrogen at a throughput of 10 l per hr (space velocity about 200) while the temperature was raised to 360°C over a period of 3–4 days, synthesis was started at 285°C and atmospheric pressure of $1H_2 + 1CO$ gas at an hourly space velocity of 100 (volumes of gas per volume of catalyst per hour).

Smith, Davis, and Reynolds [9] reported that cobalt-copper-chromium oxide showed some activity. This preparation was precipitated with sodium hydroxide from a solution containing cobaltous nitrate, chromic

[12] A. Erdely and A. W. Nash, *J. Soc. Chem. Ind.* (*London*), **47**, 219T–23T (1928).

[13] O. C. Elvins and A. W. Nash, *Fuel*, **5**, 263–5 (1926); *Nature*, **118**, 154 (1926); A. W. Nash, *J. Soc. Chem. Ind.* (*London*), **45**, 876–78 (1926).

[13*a*] O. C. Elvins, *ibid.*, **46**, 473–8 (1927).

chloride, and cupric sulfate and was reduced with hydrogen at 300°–350°C. In the activity test, the exit gas had a strong odor of hydrocarbons and a film of oil collected on the surface of the watery condensate. Similar results were obtained from cobalt-copper-uranium oxide, precipitated by potassium hydroxide from a solution containing cobaltous nitrate and cupric sulfate. To the moist cobalt-copper hydroxides filter cake was added finely divided uranium oxide prepared by decomposing uranium acetate, $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$. In the test with this catalyst, which was reduced with hydrogen at 300°–350°C, a substance resembling white petrolatum was produced in the connecting tubes.

Kodama [14] reported that the activity of cobalt-copper catalysts was enhanced by the promoters thoria and magnesia. Fischer [6] also reported the incorporation of thorium in the cobalt-copper catalyst; the ratio of constituents was cobalt:copper:thorium = 9:1:2. This catalyst was prepared by decomposition of a mixture of the nitrates and taken immediately into synthesis without preliminary reduction with hydrogen at high temperature. The highest yield obtained with this catalyst at a flow of 4 l of $2H_2 + 1CO$ gas passed over 5 g of oxides per hr was about 70 g of liquid hydrocarbons (C_5+) per cu m of synthesis gas. The approximate composition of the hydrocarbon product obtained in a double pass of $2H_2 + 1CO$ gas at a low space velocity is shown in Table 1. About 63 per cent of the gasoline hydrocarbons was in the boiling range below 100°C.

Table 1. Composition of Hydrocarbons Produced over Cobalt Catalyst at Atmospheric Pressure of $2H_2 + 1CO$ Gas

(Low space velocity; double pass of synthesis gas.)

Constituent	Per Cent (by weight)
Methane	27.4
Ethane	6.6
$C_3 + C_4$ (gasol)	10.2
Gasoline (Kogasin I)	37.6
Diesel oil (Kogasin II)	17.5
Paraffin	1.6

Cobalt-copper-manganese oxide catalysts were tested by Elvins and Nash.[13,15] The catalysts were prepared at first by thoroughly mixing the moist precipitated hydrated oxides of cobalt, copper, and manganese.

[14] S. Kodama, *J. Soc. Chem. Ind. Japan*, **32**, Suppl. Binding, 4, 6, 23, 285–6 (1929); *ibid.*, **33**, Suppl. Binding, 60, 202–3, 399–400 (1930).

[15] O. C. Elvins, *J. Soc. Chem. Ind. (London)*, **46**, 473T–8T (1927).

The mixture was filtered and then carefully dried to 150°C. It was reduced in pure hydrogen in the catalyst-testing reactor at a temperature below 400°C until no more water was produced. Passage of $1H_2 + 1CO$ gas over the catalyst at a temperature of 285°C, a space velocity of about 45 (volumes of gas per volume of catalyst per hour), and atmospheric pressure produced small quantities of not only saturated hydrocarbons but also olefins and oxygenated compounds. Subsequently, preparation of the catalysts by decomposition was reported to be preferable to precipitation. The following procedure was described for a catalyst of composition $4Co_2O_3:2CuO:3MnO_2$, parts by weight. Cobalt nitrate (211 g), copper nitrate (90 g), and manganese nitrate (102 g) were melted in their water of crystallization and dried in an oven, with stirring, at 110°C, after which the oven temperature was raised to 150°C and was so maintained until oxides of nitrogen were no longer evolved. The product (66 cc) broken in the form of 5–10 mesh granules was charged into the reactor tube. Further decomposition of residual nitrates was carried out by heating the tube to 300°C in a nitrogen atmosphere until the escaping gas did not redden litmus paper. Reduction of the catalyst took place in hydrogen at temperatures below 410°C. Synthesis at atmospheric pressure of $1H_2 + 1CO$, 286°C, and an hourly space velocity of 100 produced about 10 g of liquid and solid hydrocarbons per cu m of feed gas.

Cobalt-copper (4:1)-manganese oxide, precipitated with sodium hydroxide from a solution containing cobaltous and cupric nitrates and manganous chloride and reduced with hydrogen at 300°–350°C, was tested by Smith and coworkers.[9] The maximum yield of C_5+ hydrocarbons obtained at atmospheric pressure at a space velocity of 160 was 66 g per cu m of water gas, at a synthesis temperature of 275°C. Very heavy products, *ie*, high-melting waxes, appear not to have been present. In further tests [10] in a modified apparatus, the same catalyst was used at a lower synthesis temperature. It was compressed into pellets 8 mm in length and 2 mm in diameter and was carefully reduced in the converter, first at 150°C with hydrogen diluted with 9 times its volume of nitrogen, and then with gradually increasing temperature and concentration of hydrogen until pure hydrogen was used at 300°–325°C. After each synthesis experiment, the catalyst was reactivated with hydrogen, the temperature being gradually increased to 250°–300°C. Yields of C_5+ hydrocarbons, per cubic meter of water gas charged, were about 23 g at 240°C and a space velocity of 130, and 15 g at 260°C and a space velocity of 260. Methane constituted 30 per cent, and C_5+, 35 per cent, of the total hydrocarbon product, when synthesis was carried out at 240°C. The C_5+ product, although more saturated, was similar

to that obtained by Fischer and his coworkers from an iron-copper catalyst.[11]

The effect of alkali in producing higher-molecular-weight products had been observed when the synthol process was discovered. Addition of alkali to Fischer-Tropsch catalysts, particularly iron, constituted one of the most important steps in their development. This subject will be discussed in a later section in this chapter. The effect of addition of alkali to cobalt catalysts was similar to its effect on iron but to a smaller degree. Cobalt-copper alkalized with about 0.5 per cent potassium carbonate produced high contraction which rapidly decreased.[5] Paraffin formation was not observed for 68 hr, in contrast to 21 hr with iron catalysts. Cobalt-copper (9:1) to which was added glass powder was poorly active when tested with water gas. At 270°, the liquid product fraction was very small; at lower temperatures less methane and more liquid hydrocarbons were produced. During any one period, production fell off rapidly. The highest yield was about 33 g of C_5+ hydrocarbons per cu m of water gas, obtained at 250°C. Cobalt-copper (9:1) + 10 per cent [$Al(OH)_3 + \frac{1}{3}NaOH$] was active for only a few days when tested at atmospheric pressure and 230°C. At the end of the first day, the contraction was 40 per cent and the product contained, in grams per cubic meter of water gas, 26.7 methane, 66.0 C_1–C_4 hydrocarbons, and 39.1 C_5+ hydrocarbons.

It is apparent from the discussion in the preceding pages that the catalysts tested during the years 1925–1930 were short-lived and produced low liquid hydrocarbon yields. Unfortunately, all this early work was carried out at atmospheric pressure: at this pressure even catalysts that were later found to be active when suitably pretreated and operated at higher pressure were very poor.

100Ni:18ThO₂:100 Kieselguhr Catalyst

The precipitation of nickel-thoria on kieselguhr in 1931 was an important advance in the development of Fischer-Tropsch catalysts. The procedure of precipitation from the metal nitrate solutions produced more active catalysts than decomposition of the nitrates, and the presence of copper severely inhibited the activity of the nickel-thoria-kieselguhr catalyst. Table 2 shows the effect of composition and of nature of precipitant upon the activity of the nickel-thoria-kieselguhr catalyst.[16] Potassium carbonate used as precipitant produced the best catalyst. Sodium and potassium hydroxides produced completely inactive catalysts. Eighteen per cent thoria and a ratio of nickel:kiesel-

[16] F. Fischer and K. Meyer, *Brennstoff-Chem.*, **12**, 225–32 (1931).

TABLE 2. EFFECT OF COMPOSITION AND PRECIPITANT UPON NICKEL-THORIA-KIESELGUHR CATALYST TESTED AT ATMOSPHERIC PRESSURE WITH $2H_2 + 1CO$

(Flow of 4 l per hr per 4 g Ni; catalyst layer 30 cm long.)

Variable	Temperature, °C	Time, hr	Contraction, per cent [a]	Average C_5 + Hydrocarbons, g per cu m [b]	CO Converted to Hydrocarbons, volume per cent		
					Total	Liquids	Gases
A. Effect of precipitant on 100Ni:18ThO_2:100 kieselguhr [c]							
Precipitant							
K_2CO_3	178	90	70	84	88	65	35
Na_2CO_3	178	40	62	72	76	64	36
$KHCO_3$	180	117	48	46	60	43	57
$(NH_4)_2CO_3$	192	114	44	38	55	44	56
B. Effect of ThO_2 on 100Ni:100 kieselguhr							
% ThO_2							
18	180	355	65	74	84	63	37
24	183	355	61	68	79	61	39
12	178	138	51	49	62	55	45
C. Effect of kieselguhr on 100Ni:18ThO_2, precipitated by K_2CO_3							
Ni:Kg							
1:1	177	138	65	79	84	63	67
1:1.33	182	170	67	69	86	50	50
2:1	182	138	67	62	86	47	53
3:1	183	170	60	52	79	41	59
1:2	190	92	49	49	62	53	47

[a] 100(1 − flow out per flow in).

[b] Per cubic meter of $2H_2 + 1CO$ gas; specific gravity of oil of 0.7 is assumed.

[c] Reduced at 450°C, except $(NH_4)_2CO_3$ precipitated catalyst, which was reduced at 350°C.

guhr of 1:1 were optimum. The kieselguhr, which is a diatomaceous earth used commercially as a filter aid, had a bulk density of 0.1 after purification by extraction with hydrochloric and nitric acids. Thus, a catalyst of composition 100Ni:18ThO$_2$:100 kieselguhr, prepared under optimum conditions and reduced by hydrogen at 450°C for 3 hr, pro-

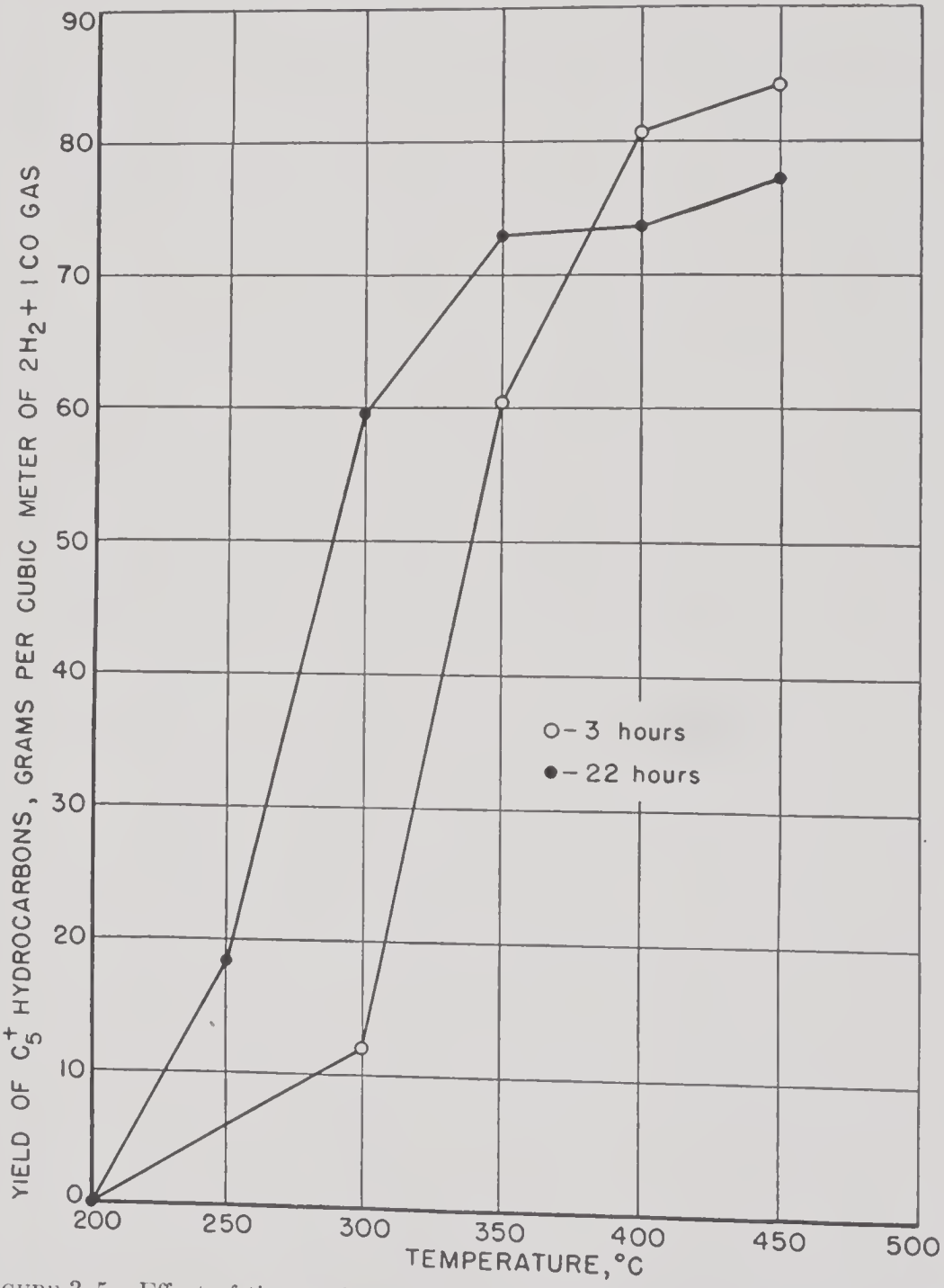


FIGURE 3–5. Effect of time and temperature of reduction upon K_2CO_3-precipitated 100Ni:18ThO$_2$:100 kieselguhr catalyst (synthesis test at atmospheric pressure and 177°C).

duced a maximum yield of 90 g of C_5+ hydrocarbons per cu m of $2H_2 + 1CO$ at 178°C, in a single pass. This catalyst was operated for 5 weeks at atmospheric pressure and produced a high conversion of carbon monoxide of almost 90 per cent, of which two-thirds was liquid and one-third gaseous hydrocarbon product. The synthesis gas had the following composition: 26–27 CO, 55–57 H_2, 3–4 CO_2, 6–7 CH_4, 7–8 N_2, per cent by volume.

If the catalyst was not reduced but was taken directly into synthesis at 180°C with synthesis gas, it was not active. The effect of temperature and length of reduction period upon the liquid hydrocarbon yield is shown in Figure 5. It was observed that reduction at 250°C for 22 hr corresponded approximately to reduction at 300°C for 3 hr. The liquid yield at this point was about 20 g per cu m of $2H_2 + 1CO$. The best catalyst was that reduced by hydrogen at 450°C for 3 hr.

The preparation of the $100Ni:18ThO_2:100$ kieselguhr catalyst was described as follows: nickel and thorium nitrates, corresponding to 5 g of nickel and 0.9 g of thoria, were dissolved together in 100 cc of water and mixed with 6 g of pure kieselguhr. The mixture was precipitated cold with the stoichiometric equivalent of potassium carbonate dissolved in 50 cc of water. The precipitate was heated quickly to boiling, filtered, and washed on the funnel with 500 cc of hot water. It was then dried in air at 110°C and pulverized. In this state, the catalyst oxide mixture was introduced into the synthesis reactor and reduced with hydrogen for 3 hr at 450°C.

$100Co:18ThO_2:100$ Kieselguhr Catalyst

Fischer did not believe that cobalt catalysts were practicable on a large scale, because of the limited availability of cobalt. Nevertheless he prepared and tested the $100Co:18ThO_2:100$ kieselguhr catalyst on a laboratory scale.[17] The method of precipitation was the same as that used for the $100Ni:18ThO_2:100$ kieselguhr catalyst; the conditions of reduction by hydrogen were 4 hr at 350°C. The best yield of C_5+ hydrocarbons obtained by Fischer from a potassium carbonate-precipitated cobalt catalyst of this composition was about 100 g per cu m of $2H_2 + 1CO$, obtained in a single pass at 195°C and atmospheric pressure. The catalyst life was about 2 months. During this period the average yield of C_5+ hydrocarbons was 82 g per cu m and the minimum yield 72 g. Distillation and other analyses showed the product to consist of paraffinic and olefinic hydrocarbons. The fraction boiling in the range 46°–185°C was about 35 per cent olefinic and the 100°–310°C

[17] F. Fischer and H. Koch, *ibid.*, **13**, 61–8 (1932).

fraction, 14 per cent. The average composition of the C_3+ hydrocarbon product, reported by Fischer,[18] is shown in Table 3. The yield of methane was smaller and the fraction of olefins in the liquid hydrocarbon product larger than were obtained from the nickel catalyst.

TABLE 3. COMPOSITION OF PRIMARY PRODUCTS OBTAINED FROM 100Co:18ThO₂:100 KIESELGUHR CATALYST

(Single stage, atmospheric pressure, synthesis gas containing CO 29 per cent and H_2 58 per cent)

Constituent	Boiling Range, °C	Melting Point, °C	Quantity, weight per cent	Olefin Content, volume per cent
Gasol ($C_3 + C_4$)	<30		4	50
Gasoline (Kogasin I)	30–200		62	30
Diesel oil (Kogasin II)	200–300		23	10
Soft paraffin [a]		50	7	..
Hard paraffin [b]		>70–80	4	..

[a] From oil.
[b] From catalyst.

When pilot-plant tests in 1933–1934 showed that nickel catalysts were unsuitable for commercial application, this 100Co:18ThO₂:100 kieselguhr catalyst of Fischer was the starting point in the catalyst development at Ruhrchemie A.G. which led to the adoption of Co-ThO₂-MgO-kieselguhr (100:5:8:200, parts by weight) as the German normal commercial catalyst. This development is described in a later section in this chapter (p 137). In 1936, the superiority of cobalt over nickel was again demonstrated, when it was observed that nickel catalysts deteriorated rapidly at synthesis pressures higher than 1 atm, through the formation of volatile nickel carbonyl.

A cobalt preparation of the same composition as Fischer's catalyst was tested in 1935 in the first laboratory and pilot-plant (4 gal per day) studies at the British Fuel Research Station, Greenwich. The objective of this work was to synthesize lubricating oils from the primary olefinic hydrocarbon products. The method used in 1937 for preparing this catalyst on the pilot-plant scale was given as follows:[19] The appropriate quantities of cobalt and thorium as the nitrates were dissolved in distilled water in the precipitation tank, fitted with a closed steam

[18] F. Fischer, *ibid.*, **16**, 1–11 (1935).

[19] *Report of the Fuel Research Board* (British), His Majesty's Stationery Office, London, Report for the year ended March 1936, p 148; Report for the year ended March 1937, pp 141–7; Report for the year ended March 1938, pp 186–97; Report for the year ended March 1939, pp 151–67.

coil for heating. Acid-washed kieselguhr was added while the mixture was vigorously stirred, and then a slight excess of cold dilute potassium carbonate solution was slowly added from the alkali tank above. When precipitation was complete, the mixture was heated to the boiling point, and then forced through the filter press by compressed air. The precipitate was washed free from alkali with boiling distilled water. Tests showed that catalysts used directly in synthesis without thorough washing were inactive. The catalyst was dried at 110°C and then broken up into 4–8 mesh granules. Approximately two-thirds of the dry catalyst was collected in this manner; the finer-grained material was powdered and pelleted. The quantity of dry catalyst prepared in a single batch was 5 kg. The capacity of the precipitation tank was 380 l, while that of the alkali tank was 130 l. For each 10 g of Co used in the preparation of the catalyst, 600 cc of distilled water was used to make up the solution, 400 cc for the potassium carbonate solution, and 2 l for washing.

In a 700-hr pilot-plant test with a batch of catalyst consisting of granules and pellets, prepared as described above and reduced by flue gases at 350°C in a unit separate from the synthesis reactor, the average oil yield (C_5+ hydrocarbons) was 60 g per cu m synthesis gas ($2H_2 + 1CO$ containing 4 per cent inerts), produced at operating temperatures between 194° and 214°C and at atmospheric pressure.

Subsequently, in 1938, the procedure of catalyst preparation was modified in two respects: (1) addition of kieselguhr was postponed until 80 per cent of the potassium carbonate had been added to the mixture of cobalt and thorium nitrates. (2) All the dried catalyst cake was pelleted, no lubricant being used. Laboratory-scale tests of this catalyst reduced by hydrogen at 350°C and operated at atmospheric pressure with $2H_2 + 1CO$ gas at a throughput of 200 cc per g catalyst per hr

Table 4. Olefinic Content of Oil from $100Co:18ThO_2:100$ Kieselguhr Catalyst at Atmospheric Pressure of $2H_2 + 1CO$ Gas (British Fuel Research Station)

Boiling Range, °C	Weight Per Cent	Assumed Mean Molecular Weight	Bromine Number	Per Cent of Mono-olefins
<80	14.9	80	100.5	50
80–110	14.8	100	57.0	35.5
110–140	10.5	114	35.3	25.2
140–210	17.3	142	17.4	15.4
210–250	11.4	172	5.4	5.8
250–300	14.7	263	0.6	1.0
Residue	14.7	...	.....	....
Loss	1.8	...	.....	....

produced yields of C_3+ products of 110–130 g per cu m of synthesis gas. A 1,900-hr pilot-plant test at 186°–215°C and atmospheric pressure, reported in 1939,[19] produced over 93 g C_5+ hydrocarbons per cu m of $2H_2 + 1CO$. Of this yield, 3 g was "catalyst wax," which was removed by solvent extraction of the catalyst at 200-hr intervals during the run. The octane number (C.F.R. motor method) of the gasoline fraction boiling below 150°C was 46. The cetene number of the Diesel oil fraction (210°–300°C) was 100. Since the olefin content of the oil was of particular interest, the degree of unsaturation of the product recovered at the end of 500 hr was determined by measuring the bromine number of various fractions. Results are shown in Table 4.

In 1942, when U. S. Bureau of Mines catalyst development was resumed after a lapse of 12 years, a catalyst of composition 100Co: $18ThO_2$:100 kieselguhr was tested.[20] Catalyst 2A was prepared by the addition of potassium carbonate solution to a cobalt nitrate solution containing the kieselguhr (Johns-Manville Hyflo-Super-Cel filter aid) and the thoria, which had been separately precipitated by potassium hydroxide. Bulk density of the pellets, compressed in a pelleting machine, was 0.69 g per cc. The catalyst was reduced in the reactor by passage of hydrogen at atmospheric pressure at a space velocity (volumes of hydrogen per volume of catalyst space per hour) of 20 for 24 hr. During the first 20 hr, the temperature was gradually raised to 360°C and was held at that point for 4 hr longer. Then the catalyst was inducted by passage of synthesis gas at 7 atm for 10 hr during which time the temperature was raised from 160°C to synthesis temperature. During a 2,400-hr test (Table 5) at 7 atm, with hydrogen flushing after every 4 or 5 days, fairly uniform activity was maintained. The average yield was about 55 g C_5+ hydrocarbons per cu m of feed gas (containing $2H_2 + 1CO$), and the maximum yield 85 g. The specific yields (grams per cubic meter of gas) in all U. S. Bureau of Mines tests were obtained at an arbitrarily chosen and fixed degree of contraction, usually 70 per cent for cobalt catalysts, per pass. In a multistage process, the specific yield would be expected to be about 50 per cent greater. Also, operation in a single pass at complete conversion would produce yields about 33 per cent greater.

By an improved method a catalyst of the same composition was prepared in 1944 [20] as follows: To a boiling solution of chemically pure cobalt and thorium nitrates of about 0.6 molarity of cobalt nitrate heated to boiling were added Johns-Manville Filter-Cel kieselguhr and then a cold solution of potassium carbonate, slightly in excess of the stoichio-

[20] H. H. Storch, R. B. Anderson, L. J. E. Hofer, C. O. Hawk, H. C. Anderson, and N. Golumbic, *U. S. Bur. Mines Tech. Paper* 709 (1948), 213 pp.

TABLE 5. U. S. BUREAU OF MINES TESTS OF PELLETED Co-ThO_2-KIESELGUHR (100:18:100) CATALYST WITH $2H_2 + 1CO$ GAS MIXTURE [a]

Catalyst No.	Total Time, hr [b]	Pressure, atm	Average Space Velocity [c]	Average Temperature, °C	Average Contraction, per cent	Hydrocarbon Products						H_2O, g per cu m [d]
						CH_4, g per cu m [d]	C_1–C_4, g per cu m [d]	Liquids and Solids, C_5+				
								Av g per cu m [d]	Max g per cu m [d]	Weight Per Cent of Total Hydrocarbons	Space-time-yield [e]	
2A	600	7	206	190	50	....	21	54 [f]	85	72	11.3	.....
	1,260		222	194	51	....	23	55	61	71	12.2	.....
	1,920		193	197	50	....	24	57	63	71	11.1	.....
	2,430		157	197	60	....	17	55	74	78	8.0	.....
108B	748 [g]	1	100	184	71	14.2	26.9	82.1	95.8	75.3	8.3	173.3
	890 [h]	7	100	189	71	23.4	40.3	83.9	97.8	67.6	8.3	176.5
	1,114 [i]	7	100	187	70	20.5	33.9	83.0	109.0	69.5	8.3	164.2

[a] Contains 2–4 per cent of inerts.

[b] At 100-hr intervals, synthesis was stopped while products were recovered and catalyst was reactivated by hydrogen passed for 2 hr at a temperature 10°C higher than synthesis temperature.

[c] Volume of feed gas per hour per bulk volume of catalyst.

[d] Grams per cubic meter of feed gas.

[e] Kilograms per cubic meter of bulk volume of catalyst per hour.

[f] Average specific gravity and bromine number of liquid product were 0.73 and 40, respectively.

[g] Catalyst was inducted by introduction of synthesis gas at 150°C and atmospheric pressure at a space velocity of 100 (STP). Within 1.5 hr temperature was raised to 175°C and was so maintained for 48 hr, then increased to 180°C and so maintained for 24 hr, and finally increased to synthesis temperature.

[h] This was continuation of test in preceding row.

[i] Catalyst was inducted by introduction of synthesis gas at 150°C and 7 atm at a space velocity of 100 (STP) for 1.5 hr. Temperature was then increased until contraction was 55 per cent at 174°C. After 48 hr, the temperature was raised to 180°C as an upper limit for 24 hr.

metric equivalent, while the mixture was efficiently stirred. The precipitate, which settled rapidly, was filtered with suction and was washed with boiling distilled water until the wash water was nitrate-free (negative test with diphenylamine-sulfuric acid reagent). The moist filter cake was spread on glass plates in layers about $\frac{1}{4}$ in. thick and dried in air at about 100°C. The dry cake was powdered, screened, and compressed in a pelleting machine into pellets 3.2 mm in diameter by 3.2 mm in length. Four per cent by weight of flake graphite was mixed with the powder to act as a die lubricant during pelleting. Bulk density of the pellets was 0.77 g per cc. The catalyst was reduced in the reactor by hydrogen at atmospheric pressure passed at a space velocity of 20 for 24 hr. During the first 20 hr, the temperature was gradually increased to 360°C and was held at that point for 4 hr longer.

In two tests of more than 1,000 hr each at atmospheric pressure and at 7 atm, respectively, this catalyst (108B) produced an average of 83 g of C_5+ hydrocarbons per cu m of synthesis gas charged (Table 5). The maximum yield was 109 g per cu m.

German Commercial Catalyst Development

100Ni:25MnO:10Al$_2$O$_3$:100 KIESELGUHR

Replacement of thorium in the 100Ni:18ThO$_2$:100 kieselguhr catalyst by manganese, which had the advantage of being less expensive, was attempted by Fischer.[16] A catalyst consisting of nickel-manganese-kieselguhr in the ratio 100:20:100 was prepared by precipitating manganese dioxide from the nitrate with hydrogen peroxide and then precipitating the whole catalyst by potassium carbonate. This catalyst was operated for 4 weeks at 190°–200°C and atmospheric pressure and produced a maximum yield of about 90 g and an average yield of about 75 g of C_5+ hydrocarbons per cu m of $2H_2 + 1CO$ in a single pass. Improvement of the catalyst was observed when a small quantity of alumina was added.

Fischer and his coworkers in 1932 considered their process sufficiently well developed on a laboratory scale to merit pilot-plant experimentation.[6,21–25] The catalyst had the following approximate composition: 100Ni:25MnO:10Al$_2$O$_3$:100 kieselguhr. It was prepared in the labo-

[21] F. Fischer, H. Pichler, and R. Reder, *Brennstoff-Chem.*, **13**, 421–8 (1932).
[22] F. Fischer, O. Roelen, and W. Feisst, *ibid.*, **13**, 461–8 (1932).
[23] R. Hartner-Seberich and H. Koch, *ibid.*, **13**, 308–10 (1932).
[24] F. Fischer and H. Koch, *ibid.*, **13**, 428–34 (1932).
[25] H. Koch and O. Horn, *ibid.*, **13**, 164–7 (1932).

ratory by dissolving, in 600 parts by weight of distilled water, 250 parts of crystalline nickelous nitrate ($6H_2O$), 50 parts of manganous nitrate ($6H_2O$), and 34 parts of aluminum nitrate ($9H_2O$). To the nitrate solution was added 60 parts by weight of kieselguhr, unpurified but sifted. The mixture was immediately precipitated cold with a solution of 210 parts by weight of anhydrous potassium carbonate dissolved in 600 parts of distilled water. The precipitate was quickly heated to boiling, filtered, washed 4 or 5 times with hot distilled water (20 cc H_2O per g Ni), and dried in a stream of air at 110°C. For laboratory tests, the dried mass was powdered. For larger-scale tests granules were obtained by pressing the wet filter cake upon the funnel in such a manner as to produce large cracks. When dry, the filter cake broke along the cracks and the granules thus obtained were screened to remove fine powder.

In preparation on a large scale, technical-grade raw materials were used.[26] A mixture of manganese dioxide (pyrolusite), aluminum scraps, and one-third of the nickel was treated with one-third of the required amount of nitric acid solution containing 1 part of concentrated acid of specific gravity 1.4 and 2 parts of water. The mixture was slowly heated for about 3 hr, until the nickel was dissolved. The remaining manganese dioxide and aluminum mixture was mixed with another portion (one-third) of the nickel and treated with a similar aliquot of nitric acid. With the final addition of the remaining nickel and nitric acid all the manganese dioxide except a small amount of impurity dissolved. The excess nitric acid was neutralized with potassium carbonate and precipitation was carried out as described above, using technical-grade potassium carbonate.

The catalyst was reduced with hydrogen in the synthesis converter for 4 hr at 450°C. This temperature could not be lowered by adding copper to the catalyst: it was observed that even very small quantities of less than 1 per cent curtailed the productivity 35 per cent.[27] Similarly, addition of carbon monoxide or carbon dioxide to the hydrogen used in reduction produced poor catalysts. However, if the catalyst was reduced at 450°C with hydrogen containing ammonia, before being taken into synthesis, an improvement of 15 per cent in yield and 13 per cent in the life of the catalyst was observed.[28] Reactivation by removal of hard paraffin from the catalyst was carried out by reducing for 4 hr at 450°C with hydrogen containing about 200 g ammonia per cu m of hydrogen. By this procedure a catalyst could be restored to its original efficiency about 6 times.

[26] F. Fischer and K. Meyer, *ibid.*, **14**, 47–50 (1933).
[27] F. Fischer and K. Meyer, *ibid.*, **14**, 64–7 (1933).
[28] F. Fischer and K. Meyer, *ibid.*, **14**, 86–9 (1933).

In laboratory tests using 15-mm-I.D. glass tubes in which 4 l per hour of $2H_2 + 1CO$ was passed over a 30-cm horizontal layer of catalyst corresponding to 4 g of Ni, the maximum yield obtained at 190°C and atmospheric pressure was 90 g C_5+ hydrocarbons per cu m of $2H_2 + 1CO$. The average yield was 84 g, and the minimum, at the end of a 4-week period, was 75 g, at 210°C. The experimental plant consisted of a battery of cells 12 mm thick by 1.2 m wide by 5 m high, immersed in an oil bath. A yield of 70 g of oil per cu m of $2H_2 + 1CO$ was obtained at 190°–210°C and at atmospheric pressure. In 1934, the Ruhrchemie A.G. erected a pilot plant of about 1,000-tons-per-year capacity at Oberhausen-Holten, Ruhr, Germany (see Chapter 4, p 337). A Ni-MnO-Al_2O_3-kieselguhr catalyst was used at 190°–210°C and atmospheric pressure. Because of difficulties encountered in operation with this catalyst, nickel catalysts were abandoned for commercial use.

COBALT-THORIA-KIESELGUHR CATALYSTS

In 1934, Roelen and Feisst resumed catalyst testing in the Ruhrchemie laboratory, starting with the cobalt catalyst of Fischer. The sodium carbonate-precipitated $100Co:18ThO_2:100$ kieselguhr S.11 catalyst tested in the Ruhrchemie laboratory produced an average yield of C_3+ hydrocarbons of 120 g per cu m $2H_2 + 1CO$ during the first 4,000 hr of its life in the "Rauxelerversuchsofen"—the reactor in which the Ruhrchemie work was done.[29] Nevertheless, changes in the kieselguhr and thoria content occurred, as an intensive effort was made to produce a less expensive catalyst suitable for commercial use. Because of the limited supply of kieselguhr S.11, another kieselguhr was found which was available in larger quantities. This was known as kieselguhr S.120. A change was also made to a more dilute catalyst by doubling the kieselguhr content. The larger percentage of kieselguhr increased the dilution of the active metal and resulted in improved activity and life of the catalyst. This effect is demonstrated by the results summarized in Table 6,[30] which showed that after 100 hr the catalyst containing 200 parts by weight of kieselguhr retained its activity for a longer period. A discussion of the function of the carrier and the effect of the nature and quantity of the carrier upon the activity of the catalyst is presented in a later section of this chapter (p 175).

The first satisfactory catalyst used in the Ruhrchemie pilot-plant units contained approximately $100Co:18ThO_2:200$ kieselguhr:2Cu,

[29] C. C. Hall and S. R. Craxford, PB 93,498 (1948), 178 pp.
[30] Ruhrchemie, March 1937, F.I.A.T. Reel K21, Frame 980.

TABLE 6. RUHRCHEMIE TESTS OF COBALT CATALYSTS AT ATMOSPHERIC PRESSURE (MARCH 1937)

A. 100Co:18ThO_2:200 kieselguhr S.120; cobalt density = 68 g per l; catalyst layer = 38.3 cm

B. 100Co:18ThO_2:100 kieselguhr S.120; cobalt density = 99 g per l; catalyst layer = 26.3 cm

(Both catalysts reduced at 400°C with space velocity of H_2–N_2 of 6,000 for 2 hr.)

Time, hr	100		200		300		400		Total	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Contraction, per cent	71	72	68	65	67	61	64	49	68	62
Oil, cc per cu m [a]	83	86	88	78	83	67	68	56	81	72
Total liquids, cc per cu m [a]	123	123	..	..	..	..	98	73	....	....
Paraffin, g per cu m [a]	...	...	..	..	..	..	..	..	19.3	15.8
Paraffin, per cent of Co	...	...	..	..	..	..	..	..	480	390

[a] $2H_2 + 1CO$.

parts by weight.[31] A commercial-size reactor was put into operation at Gewerkschaft Viktor-Rauxel in the spring of 1935. The copper-containing catalyst used in this unit was reactivated 3 times by hydrogen passed at 200°–210°C for 12 hr, so that its lifetime was increased to about 3 months. An average yield of 90 g C_5+ hydrocarbons per cu m of $2H_2 + 1CO$ gas was produced in this unit.

The catalyst was prepared from technical raw materials, starting with metallic cobalt which was dissolved in nitric acid. The solution containing the nitrates of cobalt, thorium, and copper was heated to boiling. A boiling slurry of kieselguhr was added and immediately afterwards a boiling solution containing the stoichiometric equivalent of sodium carbonate. Potassium carbonate, which produced a slightly superior catalyst, was not used because it was too expensive. Study of the order in which the slurry and precipitant were added showed that it made little difference whether both were introduced into the nitrate solution simultaneously or whether one or the other was added a few seconds earlier. The precipitated mixture was heated to boiling for 1 min and

[31] L. Alberts, private communication.

then filtered with suction. The filter cake was washed 6 times with boiling distilled water, after which it was placed on trays and dried in air at 110°C for about 24 hr until the moisture content was about 8 per cent. The dry cake was broken into 1–3-mm granules, screened to remove fine powder, and then placed in the synthesis reactor. Reduction was carried out at 220°C at a space velocity of hydrogen of 100–200 for 4–6 hr; the average extent of reduction was about 60 per cent.

The low temperature at which the catalyst could be reduced was made possible by the presence of a small amount of copper. In the absence of copper, the temperature necessary to reduce the catalyst containing cobalt was 350°–400°C.[32] Reduction under these conditions required special apparatus, which was not then available. The life of the copper-containing catalyst was exceedingly short, probably as the result of progressive alloying of cobalt with copper. When, late in 1935, a separate reduction unit was completed at Ruhrchemie, copper was eliminated from the catalyst.[31]

The standard, or normal, commercial catalyst in 1937 had the approximate composition 100Co:18ThO_2:200 kieselguhr S.120. It was reduced in thin horizontal layers by the rapid vertical flow (space velocity about 6,000) of dry hydrogen containing about 25 per cent nitrogen (from the commercial ammonia-synthesis plant) at about 350°C for 40–50 min. Because of the high price of thorium, its content was decreased to 15 per cent, based on cobalt. In 1938, the normal composition was 100Co:15ThO_2:200 kieselguhr S.120. The reduction conditions were also changed to 2 hr at 400°C and a space velocity of H_2-N_2 of 6,000 (300 l per 50 cc of catalyst per hr).[33,34] Under these conditions, 60–70 per cent of the cobalt in the catalyst was reduced to free metal.

Co-ThO_2-MgO-KIESELGUHR

In 1938, Roelen suggested that part of the thoria in the cobalt-thoria-kieselguhr catalyst be replaced by magnesia.[31] The activating effect of magnesia was explained by Roelen [35] on the basis of the similarity of its molecular volume to that of cobaltous oxide (CoO), 11.3 and 11.6, respectively, which probably results in the formation of a continuous series of mixed crystals and influences the reducibility of the catalyst. The

[32] H. Pichler, The Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen, *U. S. Bur. Mines Spec. Rept.*, 1947, 159 pp. Translation reproduced in T.O.M. Reel 259, Frames 467–654.

[33] Ruhrchemie, 1938, F.I.A.T. Reel K21, Frames 1,010–11.

[34] Ruhrchemie, F.I.A.T. Reel K21, Frames 1,098–107.

[35] C. C. Hall, S. R. Craxford, and D. Gall, PB 77,705 (1946), 60 pp; *Final B.I.O.S. Rept.* 447, Item 30.

effect of varying amounts of thoria and magnesia was studied in the following way. Each preparation was tested for 2,800 hr, starting at 185°C, treating with hydrogen after 700 hr, and again at 2,200 and 2,500 hr. The temperature was increased to 192°C at 950 hr, to 193°C at 1,900 hr, and to 194°C at 2,200 hr. The figures shown in Table 7 [29,36] are the total outputs calculated as a percentage of the output from the best sample. It is remarkable how small an amount of thoria was sufficient

TABLE 7. EFFECT OF ThO_2-MgO ON PERFORMANCE OF COBALT-KIESELGUHR (100:200) CATALYST

Weight Per Cent of Promoter		Output of Products, per cent
ThO_2	MgO [a]	
5	10	100
3	10	99
2	10	99
1	10	95
0.5	10	95
....	10	92
....	15	92
15	..	90

[a] Based on starting material.

to make a cobalt-thoria-magnesia-kieselguhr catalyst perform satisfactorily. Cobalt-magnesia catalysts were sensitive to temperature and difficult to control. The mixed catalysts containing thoria and magnesia were more satisfactory in this respect. In addition, the presence of magnesia resulted in a stronger catalyst granule. This property was important in reducing dust formation in the synthesis reactors, which causes poor distribution of gas and the production of "hot spots." [37] The presence of thoria reduced to a certain extent the harmful effect of impurities, such as copper, calcium, and aluminum, and the deleterious effect of vigorous mechanical treatment of the wet catalyst cake (after filtration and washing).

The composition finally adopted for the commercial plants was 100Co: $5ThO_2$:8MgO:200 kieselguhr. This catalyst was used until 1944, when production was sharply curtailed as a result of intensive bombing of the plants. The usual variation in composition was within the limits 4.9–5.2 per cent of ThO_2 (based on metallic cobalt) and 7.5–8.5 per cent MgO.[29] The figure for magnesia was not critical and could vary between 6 and 10 per cent. However, the quantity of thoria was required to be

[36] Ruhrchemie, F.I.A.T. Reel K21, Frame 1,104A.

[37] H. V. Atwell, A. R. Powell, and H. H. Storch, *Fischer-Tropsch T.A.C. Rept.* SnMc 1 (1945), 41 pp; PB 2,051.

about 5 per cent because of its role as protector against impurities. The same composition was found to be best for both atmospheric- and medium-pressure synthesis and to produce catalysts that had a life of about 6 months. An analysis made in 1943 [31] showed the following characteristics (Table 8) for a typical catalyst batch. The average yield was 150 g per cu m of $2H_2 + 1CO$, of hydrocarbons ranging from propane-propylene to waxes of 2,000 molecular weight.

Table 8. Analysis of a Typical Commercial Cobalt Catalyst ($100Co:5ThO_2:8MgO:200$ Kieselguhr)

Granule size, mm	2–3
Dust content, per cent	1.5
Abrasivity, per cent	18.2
Bulk density, g per l [a]	280
Chemical composition, per cent	
Co	24
ThO_2	1.25
MgO	1.84
Kieselguhr	42.83

[a] Measured in converter.

MANUFACTURE OF COMMERCIAL CATALYST, $100Co:5ThO_2:8MgO:200$ KIESELGUHR

The standard Ruhrchemie cobalt-thoria-magnesia-kieselguhr catalyst was made in three catalyst-manufacturing plants.[38,39] These were Ruhrchemie at Sterkrade-Holten, Brabag at Ruhland-Schwarzheide, and Wintershall at Luetzkendorf; they produced 50.0, 32.5, and 17.5 per cent, respectively, of the total catalyst output. The Ruhrchemie plant was built during the summer of 1935, the Brabag plant in 1937, and the Wintershall factory soon afterwards.[31]

Procedure for Preparing Catalyst Cake

Maximum daily output of the Ruhrchemie Sterkrade plant was that equivalent to 4 metric tons of cobalt. This plant supplied all six Fischer-Tropsch plants in the Ruhr area. Illustrated diagrammatically in Figure 6 [37,40] are the various steps in the manufacture of the catalyst at

[38] E. H. Reichl, U. S. Naval Technical Mission in Europe, *Rept.* 248–45 (1945), 128 pp; PB 22,841.

[39] K. Gordon *et al.*, Report on the Petroleum and Synthetic Oil Industry of Germany, *B.I.O.S. Overall Rept.* 1 (1947), pp 82–103.

[40] C. C. Hall and V. Haensel, C.I.O.S. File XXVII-69, Item 30 (1945), 97 pp; PB 415.

Sterkrade. A solution (750 l) of the nitrates in the proportions equivalent to $100Co:5ThO_2:10MgO$ and containing 40–41 g per l cobalt was heated to 100°C in an overhead, stainless-steel tank (*A*). Magnesium was incompletely precipitated under the conditions of preparation, and for this reason the nitrate corresponding to 2 parts MgO in excess of that

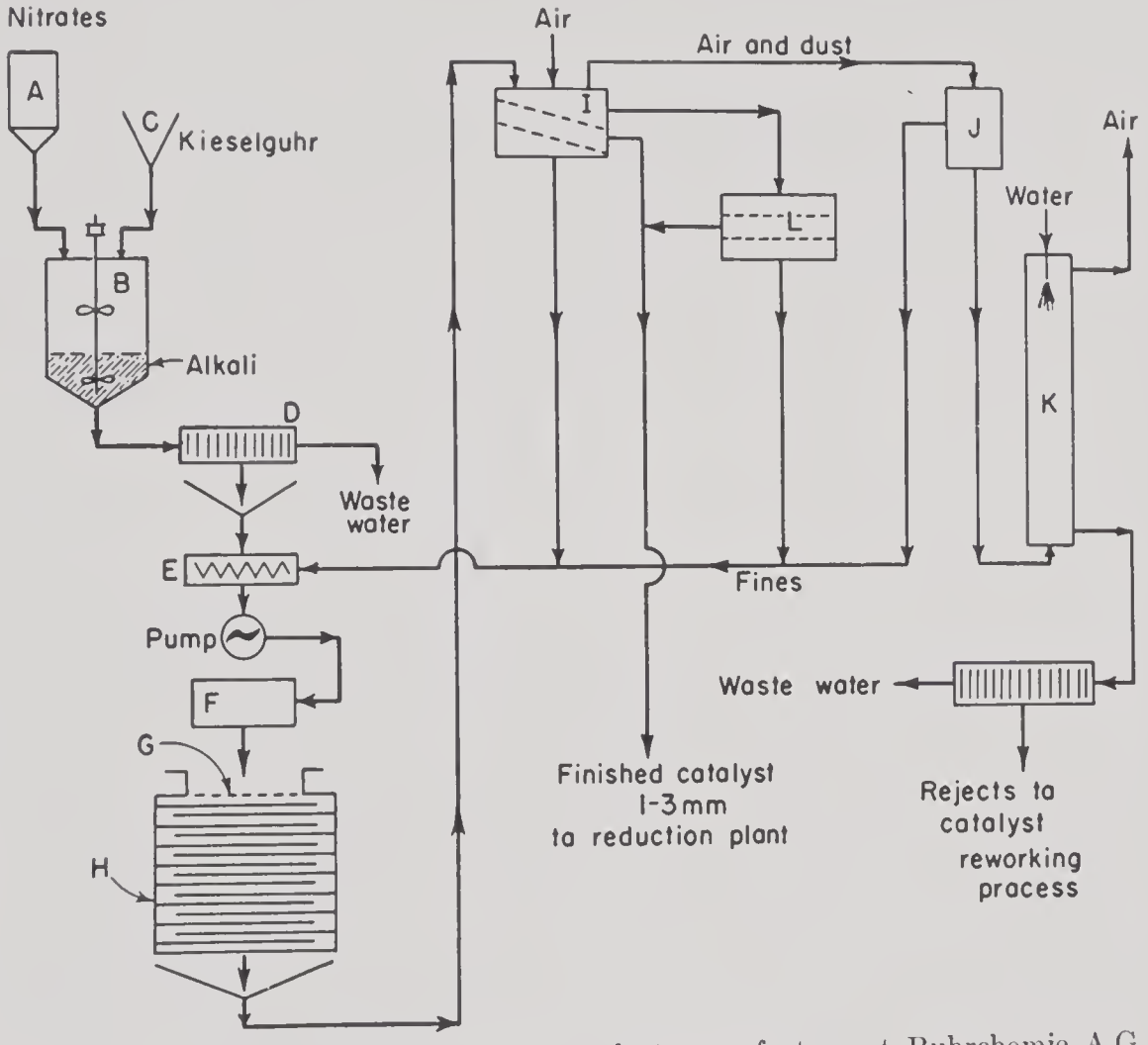


FIGURE 3–6. Flow scheme for cobalt-catalyst manufacture at Ruhrchemie A.G., Sterkrade. Reproduced from reference 40.

required in the catalyst was used. The hot nitrate solution was transferred into the precipitating tank (*B*) fitted with a direct-drive, twin-screw stirrer and containing 750 l of a solution of sodium carbonate (104 g per l) previously heated to 100°C. The mixture was stirred for 0.5 min and then dry kieselguhr (180–200 parts by weight, based on cobalt) was added through the hopper (*C*); stirring was continued for 1 min longer. Alberts [31] reported that essentially the same results were obtained by adding the sodium carbonate solution to the nitrate solution, and the kieselguhr in a hot slurry simultaneously with or a few seconds earlier or later than the precipitant. The slurry was pumped to a

standard-type filter press (*D*) and the cake washed with distilled water until the wash water was neutral when tested with nitrophenol. (In the test, 100 cc wash water was acidified first with 5 cc 0.1 *N* sulfuric acid.) Catalyst equivalent to 64 kg cobalt required about 10 cu m wash water, and the washing period was 14–15 min.

The washed cake was then dropped into a "masher" (*E*), situated below the press, and was mixed with fine powder from the screening plant. The resulting cream was pumped to a rotating suction filter (*F*). The thin cake scraped off the filter drum contained approximately 70 per cent water. It was dropped into the extruder (*G*), where rotating arms forced the paste through 3-mm-diameter holes into the drying chamber (*H*). The dryer was a cylindrical vessel 7 m in diameter, containing 20 superimposed stages 20 cm apart. The catalyst was swept around each stage by rotating arms and was dropped downward from stage to stage during a period of 1.5–2 hr. Drying was carried out by a blast of air heated by steam, until the granules contained 6–8 per cent moisture. There was no special merit in having this quantity of moisture present. It was specified only in order to discourage drying at too high a temperature, which rendered the catalyst difficult to reduce under the standard reduction conditions. Catalysts containing 200 parts of kieselguhr were best dried at about 120°C. Preparations containing less kieselguhr were oxidized more easily. This effect was observed particularly in the 100Co:15Mn:12.5 kieselguhr catalyst (described in a later section in this chapter, p 195), but it should be noted that the manganese may have catalyzed the oxidation by acting as an oxygen carrier.

Shaping the Catalyst

From the final stage of the dryer, the rough granules, containing 6–8 per cent moisture, were carried by a conveyor to the vibrating screens (*I*) from which four fractions were obtained: granules larger than 3 mm, 1–3-mm granules, fines, and catalyst dust. The dust was removed in an air current which was filtered through a cloth filter (*J*) and then scrubbed with water and steam (*K*). The catalyst dust thus recovered was not returned to the masher for inclusion in the final catalyst. This material, which represented only 0.1–0.2 per cent of the whole, was sent to the catalyst-regeneration plant and treated as spent catalyst. The fines from the screens and cloth filters, representing about 30 per cent of the product, were returned to the masher. Roelen [35] reported that if the fines were not returned immediately to the process, they deteriorated, possibly as a result of oxidation from the cobaltous to the cobaltic state, or of adsorption of carbon dioxide or water, the cobalt catalyst being

sensitive to moisture. The fraction consisting of particles larger than 3 mm passed to another set of screens (*L*), where rotating arms forced the granules through the 3-mm screen. Dust and fines obtained from this screening were returned to the masher. The 1–3-mm granules were collected from both screenings and bagged for transport to the adjacent reduction plant by a conveyor. About 20 per cent of this fraction was 1–2-mm granules and the rest 2–3-mm granules. For atmospheric-pressure reactors, either size or a mixture of the two could be used; in the medium-pressure, double-tube reactors, a mixture was undesirable because the particles of different sizes tended to become segregated.

The bulk density of the granules was 330 g per l. On a laboratory scale, the bulk density was always 10 per cent lower. According to Roelen,[29] the bulk density of the finished granules was of great importance for satisfactory reduction of the catalyst. Production of a high bulk density, which was undesirable, was influenced by the following factors: (1) increased quantity of fines incorporated in the catalyst; (2) nature of kieselguhr (Table 21), Glühguhr producing a denser catalyst than Röstguhr; (3) long and rigorous treatment during mixing of the precipitate and drying of the filter cake.

Improvement in the method of producing granules in order to obtain harder, but not denser, particles was studied.[29,35,38] "Eirichkorn" catalyst, consisting of little balls formed by simultaneous drying and slow stirring, was very hard but too dense and produced a large quantity of methane. The "Fadenkorn" catalyst was prepared by extrusion of the moist filter cake through an orifice. Blocking of the orifice by sedimentation of the kieselguhr was prevented by an oscillating shutter, moving sufficiently slowly to avoid breaking up the original gel structure. The catalyst paste was fed to the orifice by a series of paddle wheels, and the extruded thread was dried on a conveyor belt by hot air. It was then passed downward in a vertical cylinder fitted with baffle plates and with a special stirrer which threw the catalyst against the walls of the cylinder. By this procedure, granules with rounded ends were obtained and only 10–15 per cent of fines was produced. Improved gas distribution in the reactor and easier emptying of the catalyst chamber were obtained with the Fadenkorn catalyst. Roelen thought it impracticable to make thread finer than 5–6 mm satisfactorily on a commercial scale; however, at Wintershall, the Fadenkorn catalyst was made on a large scale.

The "Schiffchen" catalyst, so called because the final pieces were shaped like small boats, was the most satisfactory form. In 1947, Gehrke[41] reported that a completely new system was installed at

[41] H. Hoog, Additional Information on Various Catalytic Processes in Western Germany (British Zone)-I, *B.I.O.S. Misc. Rept.* 112 (1947), pp 1–7, 35–7.

Sterkrade to shape the catalyst in this manner in full-scale catalyst preparation. On a pilot-plant scale, the machine consisted of a drum 2 m in length and 1.5 in diameter, around the outside of which was wound alternately serrated and unserrated strips of iron. Thus, a large number of cells about 2 by 2.5 mm in size were formed. Catalyst paste was squeezed into these cells at the lower part of the drum. As the drum rotated slowly (0.1 rpm) and continuously, catalyst granules were carried up, dried at the top by hot air, and, having contracted slightly (10 per cent) during drying, were blown out by an air jet and collected on a continuously moving belt which followed a downward spiral through a heated space in which they were dried to the desired degree. The serrated strips extended all the way around the drum, whereas the unserrated ones extended only around the lower third of the circumference and did not rotate with the drum. As a result, the cells containing the catalyst were open at the sides during the drying at the top of the drum. Only 5–10 per cent of fines was produced by this procedure. The Schiffchen catalyst was hard, probably because little dust was incorporated in the catalyst paste, and showed only 6–8 per cent attrition during preliminary tests, as compared with 12–16 per cent for catalysts shaped in the conventional manner.

Reworking of Spent Catalyst

At each Fischer-Tropsch plant in western Germany, spent catalyst was extracted with product oil. One-half to 5 per cent paraffin wax and 1–2 per cent of carbon remained on the catalyst mass, which was returned to Sterkrade for reworking. In this process (Figure 7),[37,40,41] the spent catalyst containing principally cobalt, cobalt oxide, magnesium oxide, thorium oxide, and kieselguhr was treated with nitric acid. All the constituents were dissolved except the kieselguhr, which was removed by filtration and discarded. The filtrate (*A*) containing 60 g Co per l was partially neutralized with sodium carbonate solution to a *p*H of 5.8. An iron-thorium sludge ("Vorfällschlamm" or "Thor-Eisenschlamm") was precipitated, which contained iron and thorium in the ratio of 3:1, in parts by weight. The filtrate (*B*) obtained by removal of the iron-thorium sludge from the mixture consisted of the nitrates of cobalt, magnesium, and calcium. Sodium fluoride equivalent to the calcium plus 40 per cent of the magnesium was added to this filtrate. The calcium and magnesium fluorides thus precipitated were separated by filtration from the nitrate solution of cobalt and the remaining magnesium. This solution contained enough cobalt (45 g per l) so that it was ready for the catalyst-preparation plant; magnesium nitrate was added

to increase the magnesium concentration to a value equivalent to 80 g MgO per l. Precipitate (*B*), containing the iron-thorium sludge, was dissolved in sulfuric acid. Addition of potassium chloride precipitated the double salt, thorium-potassium sulfate, which was separated from the iron solution by filtration and then dissolved by treatment with sodium carbonate solution (50 g per l). The thorium solution thus obtained was

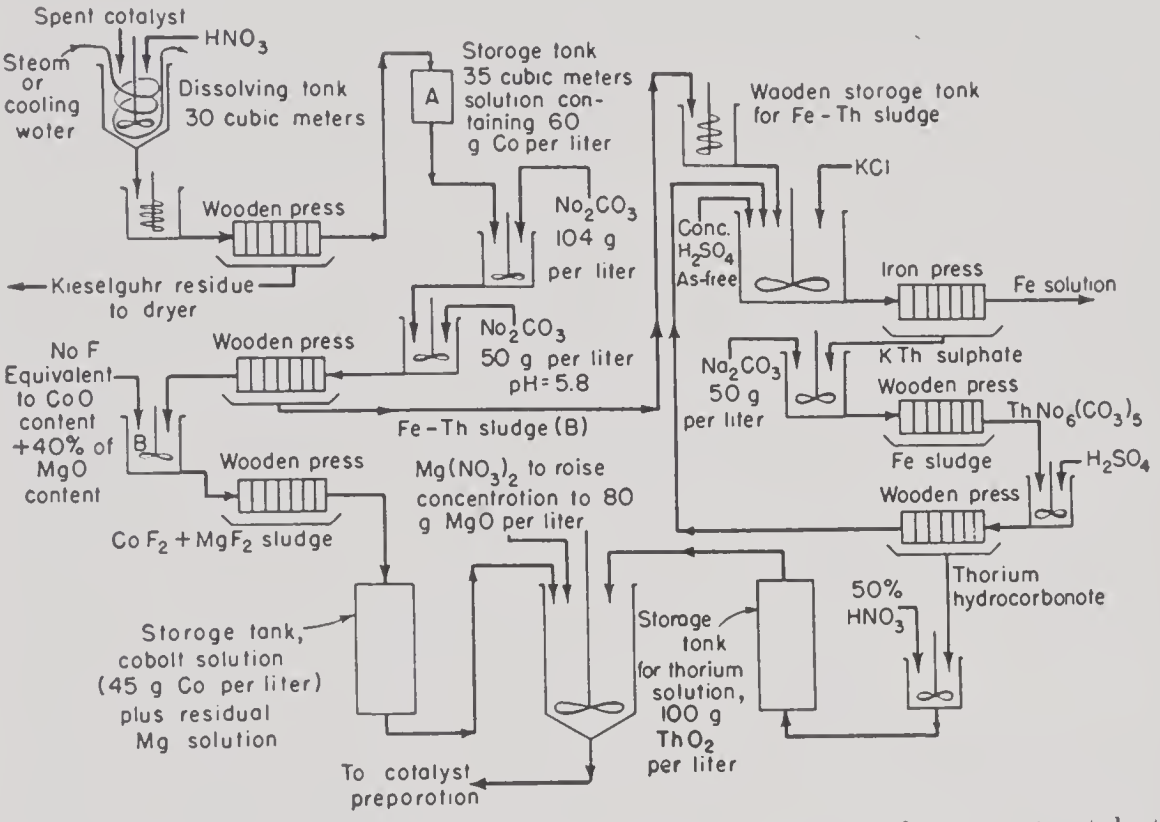

Spent catalyst
HNO_3
Steom or cooling woter
Dissolving tonk 30 cubic meters
Storoge tonk 35 cubic meters solution containing 60 g Co per liter
A
Wooden storoge tonk for Fe-Th sludge
KCl
Wooden press
No_2CO_3 104 g per liter
Conc. H_2SO_4 As-free
Iron press
Fe solution
Kieselguhr residue to dryer
No_2CO_3 50 g per liter pH=5.8
Wooden press
No F Equivalent to CoO content +40% of MgO content
B
Fe-Th sludge (B)
No_2CO_3 50 g per liter
K Th sulphate
Wooden press
$ThNo_6(CO_3)_5$
Fe sludge
H_2SO_4
Wooden press
$Mg(NO_3)_2$ to roise concentrotion to 80 g MgO per liter
$CoF_2 + MgF_2$ sludge
Thorium hydrocorbonote
50% HNO_3
Storoge tonk, cobolt solution (45 g Co per liter) plus residual Mg solution
Storage tonk for thorium solution, 100 g ThO_2 per liter
To cotalyst preporotion

FIGURE 3–7. Flow scheme for recovery of cobalt and thorium from spent catalyst at Ruhrchemie A.G., Sterkrade. Reproduced from references 40 and 41.

filtered to remove the iron impurity. Addition of a controlled quantity of sulfuric acid to the filtrate precipitated thorium bicarbonate, which was dissolved with 50 per cent nitric acid. The solution, containing 100 g ThO_2 per l, was then ready for use in catalyst preparation. Treatment of the double salt, thorium-potassium sulfate, at 90°C with concentrated sodium carbonate solution (200 g per l) until the *p*H was 7.5–8.0 produced a precipitate of thorium bicarbonate, according to one Ruhrchemie patent application.[42] However, this precipitate probably contained more iron impurity than the thorium bicarbonate obtained by the preceding method. Upon being interrogated in 1947, Gehrke [41] stated that the following procedure was used to recover the thorium from the iron-thorium sludge: The "Schlamm" was made into a slurry

[42] Ruhrchemie A.G., Patent Applic. R102,874 IV b/12m (9), July 1, 1938; F.I.A.T. Reel K21, Frames 806–7.

in a solution of sodium carbonate, and carbon dioxide injected. The thorium dissolved as a thorium-sodium double carbonate, which was filtered to remove the iron impurity, and then was pumped to the catalyst-preparation section for use in new catalyst. A cobalt-magnesia solution of the required concentration was added, and immediately afterwards the kieselguhr was introduced.

The Wintershall catalyst factory used essentially the same method as Ruhrchemie,[29] but at the Brabag plant the following procedure was adopted. The used catalyst was dissolved in nitric acid, and the kieselguhr removed by filtration. Iron and calcium were precipitated from the filtrate and separated by filtration. The cobalt was then precipitated by sodium carbonate and redissolved in nitric acid. Although this method required twice the amount of nitric acid used by the Ruhrchemie procedure, the Brabag chemists thought that their method of precipitating and redissolving the cobalt was superior in that organic impurities were removed. A comparative test made at Ruhrchemie on the two methods was reported to have given inconclusive results.

At the small Courrière-Kuhlmann Fischer-Tropsch plant at Harnes, France, which had been operated since June 1937,[43] spent catalyst was reworked by a slightly different procedure. The catalyst was treated with 3–5 per cent nitric acid. All the constituents were dissolved except kieselguhr, which was removed by filtration (*A*) and discarded. The filtrate (*A*) was neutralized with sodium carbonate to a *p*H of 4.2. This precipitated thorium, magnesium, and iron carbonates, which were separated from the solution of cobalt nitrate and the calcium nitrate impurity by filtration (*B*). The filtrate (*B*) was treated with sodium fluoride, precipitating calcium fluoride, which was removed from the cobalt nitrate mother liquor by filtration. The latter was then ready for use in catalyst preparation. The thorium, magnesium carbonate precipitate (*B*) was dissolved in sulfuric acid, and upon the addition of a controlled quantity of sodium hydroxide, magnesium and ferric hydroxides were precipitated. These were removed by filtration. The thorium solution contained a double salt, thorium-sodium sulfate, which upon heating to 80°C was hydrolyzed, precipitating thorium hydroxide. The thorium salt, after washing, was dissolved in nitric acid and the solution sent to the catalyst-preparation plant.

At Ruhrchemie, a method of preparing catalysts from solutions of sulfates had been developed.[44] These catalysts were reported to be satisfactory, provided the precipitate was washed carefully with dilute alkali. The method was not used by Ruhrchemie but was suggested for

[43] R. C. Aldrich, *Natl. Petroleum News*, **37**, R922–4 (1945).
[44] Ruhrchemie, Patent Applic. R104,999, April 15, 1939.

firms that had no cheap source of nitric acid. However, U. S. Bureau of Mines tests have indicated that sulfates are not suitable as raw materials for preparation of Fischer-Tropsch catalysts.

The overall yearly consumption of cobalt for the Fischer-Tropsch plants in Germany was between 85 and 95 tons. Before World War II, most of the cobalt was imported from the Belgian Congo. Early in the war, this supply was cut off and Finland became the only supplier of the metal. Losses in handling in the synthesis and during reworking averaged about 5 per cent. When the cobalt supply became critical, catalyst manufacturers had to resort to the recovery of cobalt from cobalt carbonate obtained as secondary product from other plants. The average thoria loss was about 16 per cent.

Reduction

The flow scheme for large-scale reduction of the standard cobalt catalyst at the Ruhrchemie Sterkrade plant is shown in Figure 8.[37,40]

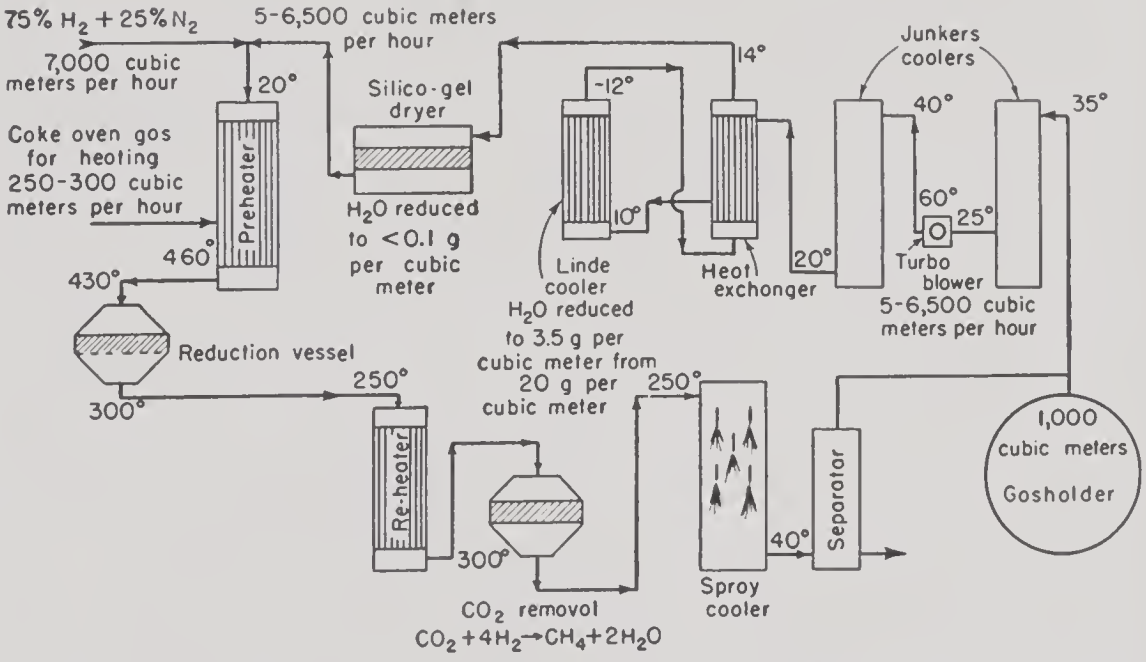


Figure 3–8. Flow scheme for commercial-scale cobalt-catalyst reduction at Ruhrchemie A.G., Sterkrade. Reproduced from reference 40.

Reduction conditions were kept constant by fixing the cobalt content, or cobalt density, during preparation at a constant value of 80 g per l of unreduced catalyst. The reduction vessel, of which there were six at Sterkrade, comprised a central compartment of square cross section containing the catalyst in a bed 30–35 cm deep and 2.1 sq m in area, with top and bottom fittings in the form of truncated pyramids (Figure 9). A

sheet-iron grill of 15-cm cubes for the purpose of breaking up the gas stream entering the reduction vessel was placed on top of the bed, sinking into it to a depth of about 10 cm. Each reduction vessel contained about 700 l of catalyst.

During reduction, a rapid stream of dry hydrogen, containing 25 per cent nitrogen (synthesis gas from the ammonia plant) and preheated to

FIGURE 3–9. Cobalt-catalyst reduction vessel at Ruhrchemie, Sterkrade.

460°C in a tubular heater fired with coke-oven gas, was passed through the reduction vessel at an inlet temperature of 430°C. The outlet temperature was 300°C, and the bed temperature probably 400°C. The space velocity measured in volumes per volume of catalyst per hour was 10,000; measured in liters per gram of cobalt per hour, it was 125. The period of reduction was about 50 min. Carbon dioxide present in the effluent gas (about 2 g per cu m) was converted to methane at 300°C by passage through a bed of synthesis catalyst contained in another reduction vessel. The gas was then cooled, dried by refrigeration, and passed through silica gel. It was returned to the preheater for recirculation. The extent of reduction was determined by measuring the volume of hydrogen evolved when a sample was treated with acid.[45]

[45] F. Martin and F. Johnswig, German Patent 720,107, Apr. 2, 1942; U. S. A.P.C. SN 240,150; Ruhrchemie, A.G., French Patent 845,301, Aug. 18, 1939.

After reduction, the catalyst was cooled to room temperature by purging the vessel with nitrogen, which was displaced by carbon dioxide either at room temperature or below. The contents of the reduction vessel were discharged into a Kübel for transport to the synthesis plant. The reduction vessels were so balanced that, after removal of the top cover plate, they could be inverted by a hand-operated mechanism. The capacity of one Kübel (Figure 10) was about 3 metric tons of catalyst.

FIGURE 3–10. Kübel for transportation of reduced cobalt catalyst to synthesis plant.

Slight variations from this reduction procedure occurred in the other two catalyst-manufacturing plants.[29] At Brabag, 90 per cent hydrogen was used; hence, the temperature was lower (360°–370°C) than at Ruhrchemie. After reduction, the Wintershall plant lowered the hot catalyst into a box cooled externally by circulating cold water and cooled it in this manner while maintaining a slow circulation of nitrogen over the catalyst.

LABORATORY TESTS

Samples of each large-scale batch of catalyst from the manufacturing plant and from the reduction plant were tested for activity.[29,35] The sample from the manufacturing plant was reduced in a separate apparatus for 2 hr at 450°C with $75H_2:25N_2$ at a flow rate of 75 l per g Co per hr or at 400°C with relatively pure hydrogen. In the laboratory at Ruhrchemie, Sterkrade, there were about 100 small catalyst-testing units with aluminum-block furnaces, which were similar to those used by Fischer at the Kaiser Wilhelm Institut für Kohlenforschung.[40] The aluminum-block furnace was heated electrically or by gas to 185°C and controlled at this temperature by a regulator. Eight samples could be tested simultaneously in the furnace. The reduced catalyst was tested with synthesis gas ($2H_2 + 1CO$ mixture containing 18–20 per cent of

TABLE 9. TEST DATA FOR A SAMPLE OF COMMERCIAL COBALT CATALYST

(Atmospheric-pressure test at 185–186°C; synthesis gas $2H_2 + 1CO$ containing 18–20 per cent inerts; flow rate 1 l per g Co per hr.)

Cumulative Time, hr	Contraction, per cent	C_5+ Hydrocarbon Product, cc per cu m [a]	
		Liquid at Room Temperature	Total [b]
4	70	..	...
18	72	98	...
56	72	89	...
80	69	94	...
128	70	70	114
176	65	77	...
223	66	76	95
272	60	75	...
319	67	69	120
368	66	62	...
416	66	73	125
464	66	67	...
511	64	56	103
559	65	60	...
607	63	63	111
655	60	66	...
703	58	62	114
753	61	64	...
	Catalyst treated 20 hr with $75H_2:25N_2$		
767	70	..	...
785	70	75	...
849	63	68	...
896	65	65	119
945	64	60	...
992	61	63	104
1,041	62	59	...
1,089	61	62	115
1,137	61	63	...
1,185	63	63	117
1,233	61	60	...
1,287	61	60	100
1,329	60	57	...
1,376	63	58	108
1,425	60	52	...
1,469	57	58	94
1,517	54	49	...
1,565	59	49	88
1,613	56	47	...

[a] Per cubic meter of synthesis gas.

[b] Liquid at room temperature plus C_5+ from activated-charcoal trap recovered by steaming at 150°C and 15–20 mm Hg.

inerts) in a 12-mm-I.D. glass tube in a bed length of about 30 mm, corresponding to a weight of cobalt of about 4 g. An active catalyst at first produced chiefly methane and a gas contraction of 55–60 per cent; after about 24 hr, production of liquid hydrocarbons began and contraction rose to 70–75 per cent. The tests were carried out usually for 500 hr. At this point, the contraction was 65 per cent. The average yield for

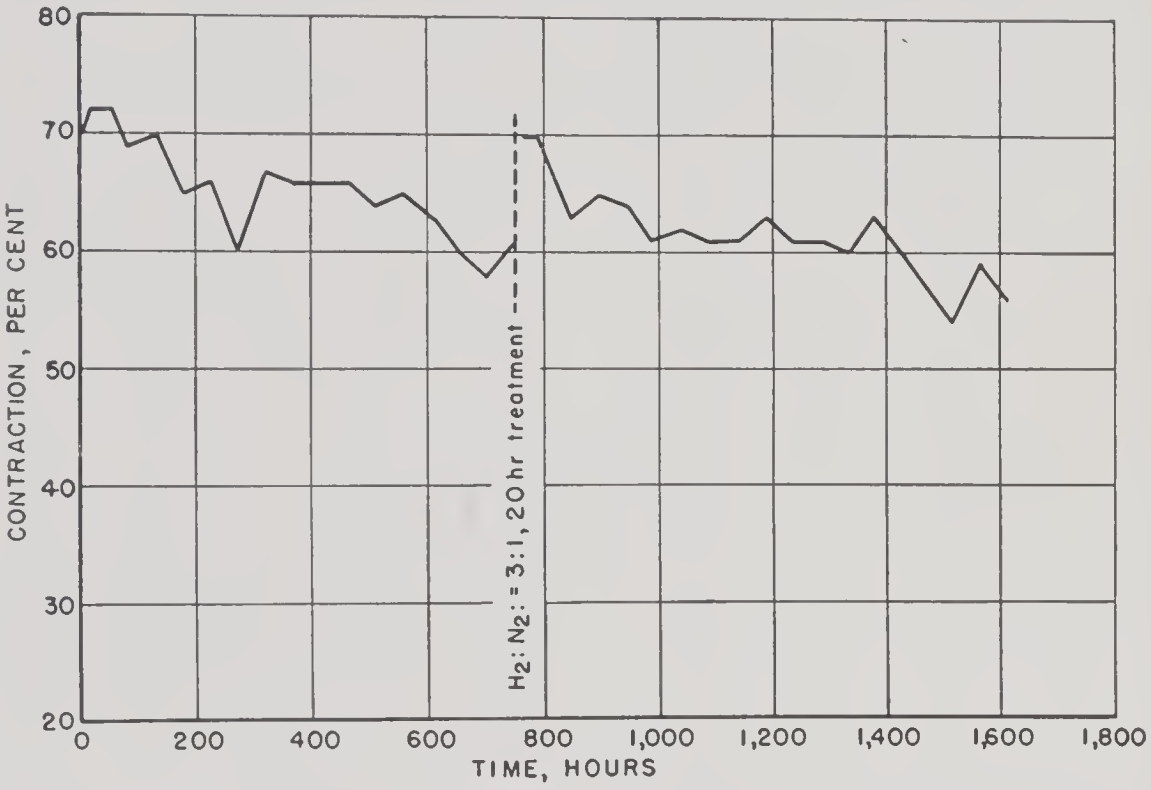


FIGURE 3–11. Cobalt-catalyst contraction curve for test run at atmospheric pressure at Ruhrchemie, Sterkrade. Reproduced from reference 46.

the whole period was 90 g C_5+ per cu m of synthesis gas. At a later period, fewer tests were made but they extended for 3 months. Table 9 shows typical laboratory test data, and Figure 11 the contraction versus time curve for a sample of commercial cobalt catalyst.[46]

Table 10 contains the results of laboratory tests of the standard commercial catalyst at 1 and 7 atm. The product distribution and properties of the various fractions are shown. These data were obtained from the Ruhrchemie files [47] and reproduced by Pichler [32] with minor changes.

[46] W. F. Faragher *et al.*, Supplemental Report on Ruhrchemie A.G., Sterkrade-Holten (Oberhausen-Holten) Ruhr, PB 1,366; *C.I.O.S. Rept.* XXXII-96, Item 30 (1946), 92 pp.

[47] T.O.M. Reel 33, Bag 3,440, Target 30/5.01, Items 23 and 24.

TABLE 10. PRODUCT FROM $100Co:5ThO_2:7.5MgO:200$ KIESELGUHR CATALYST AT 175°–200°C AND AT (a) ATMOSPHERIC, (b) 7 ATM PRESSURE OF $2H_2 + 1CO$ GAS, 18–20 PER CENT INERTS

Fraction	Grams per Cubic Meter $2H_2 + 1CO$ gas		Weight Per Cent of Liquids Plus Solids		Density, 150°C		Olefins, volume per cent		Pour Point, °C		Cooperative Fuel Research Committee Octane No.		Cetane No.	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
$C_1 + C_2$	26	21	..	..	.....	.	..	..	..	..	..	..	...	...
$C_3 + C_4$	24	17	..	..	.....	..	50	30	..	..	..	..	...	...
C_4–C_{10}	70	51	56	35	0.689	0.685	37	20	..	..	52	28	...	...
C_4–C_{11}	77	58	62	40	0.693	0.689	34	18	..	..	49	25	...	...
C_{11}–C_{18}	41	51	33	35	0.760	0.760	15	10	−18	−7	..	..	100	100
C_{12}–C_{19}	34	51	27	35	0.766	0.766	13	8	− 9	−2	..	..	100	105
Soft wax	10	36–43	8	25–30 [a]	0.900	0.900	..	..	..	..	..	..	...	...
Hard wax	4		3		0.930		..	..	..	.	..	..	...	...

[a] Higher percentage of wax may be obtained from Co-Mn catalysts at 165°–168°C and 10 atm, but with no increase in Diesel oil yield (see Table 34).

Cobalt and Nickel Catalyst Studies

REPRODUCIBILITY OF CATALYST PREPARATIONS AND TESTS

The various preparations of Co-ThO_2-MgO-kieselguhr catalyst No. 89 studied in the Bureau of Mines research and development laboratory of the Office of Synthetic Liquid Fuels, U. S. Department of the Interior, were made in the same way.[20,48] The quantities of starting materials were calculated to produce a catalyst of composition 100Co:6ThO_2:12MgO:200 kieselguhr. A solution of chemically pure cobalt and thorium nitrates of about 0.68 molarity of cobalt nitrate was heated to boiling. A boiling slurry containing kieselguhr and finely divided chemically pure magnesia and a boiling solution of sodium carbonate were added simultaneously to the solution of the nitrates. The solution was efficiently stirred and the precipitation completed as rapidly as possible. The precipitate settled rapidly. It was filtered and quickly washed free of byproduct electrolytes with boiling distilled water. The moist filter cake was spread on glass plates and dried in air at about 100°C. For granular catalysts, the dried cake was broken into pieces of 6–10 mesh size. Pelleted catalysts were compressed from finely broken filter cake in a pelleting machine and contained 4 per cent by weight of finely divided graphite added as a die lubricant. The pellets were cylinders approximately 3.2 mm in diameter and 1.6 mm in length.

The percentage of cobalt in some of the preparations was fairly constant, as follows: 89K 24.6, 89O 24.3, 89Q 23.8. The magnesia content varied because of the high solubility of magnesium oxide and carbonate. Some values of thoria and magnesia, expressed as per cent by weight of cobalt, were obtained by chemical analysis and are shown in Table 11.[48]

Table 11. Thoria and Magnesia Content of Co-ThO_2-MgO-Kieselguhr Catalysts (U. S. Bureau of Mines)

Catalyst No.	Per cent by weight of Co	
	ThO_2	MgO
89H	7.6	11.4
89V	8.3	10.3
89Z	7.0	8.5
89BB	6.3	12.1
89EE	6.1	12.5
112A	6.2	8.1

[48] R. B. Anderson, A. Krieg, B. Seligman, and W. E. O'Neill, *Ind. Eng. Chem.*, **39**, 1,548–54 (1947).

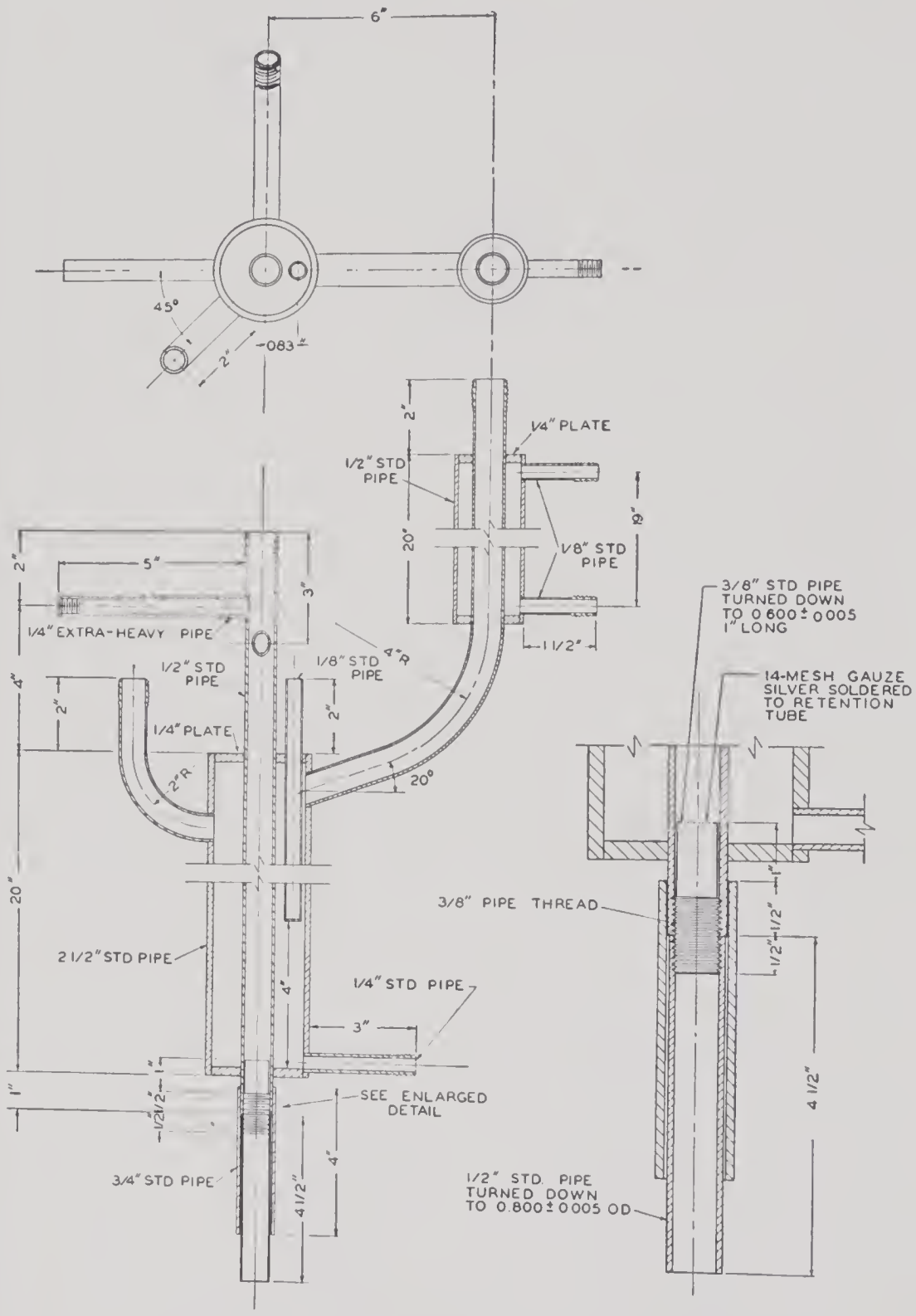


FIGURE 3–12. Single-tube converter (modified Downs type). Reproduced from reference 49.

Catalyst 112A was similar to the 89 type, except that the magnesia was precipitated from magnesium nitrate before being added to the cobalt-thorium nitrates.

Tests of the same preparation of a catalyst were reproducible, but tests of similar preparations showed considerably wider variations in activity and product distribution. The widest variations within a test were found in the data for liquid hydrocarbons because of the difficulty of recovering small quantities of liquids (70–80 cc) from two metal traps and the charcoal scrubber. The reactor and auxiliary apparatus used for catalyst testing at the U. S. Bureau of Mines from 1942 on are shown in Figures 12, 13, and 14, and photographs of the laboratory are shown in Figures 15 and 16.[48–50] The reactor consisted of standard iron pipe of 1.52-cm I.D. welded into a jacket of 6.35-cm standard pipe, the total converter length being about 50 cm. In the inner tube, containing a steel thermocouple well of 0.65-cm O.D., was a 30-cm catalyst bed. The annular space held about 50 cc of catalyst supported about 6 in. from the bottom of the converter by a wire screen. The catalyst tube was heated externally by a fluid such as tetralin for temperatures from 150° to 210°C and Dowtherm A from 200° to 400°C, boiling under constant pressure and thus maintaining constant temperature in the catalyst. The liquid-vapor bath was heated electrically by a resistance winding on the outside of the 6.35-cm jacket. Temperatures were measured by a chromel-alumel thermocouple placed within the well at the midpoint of the length of the catalyst bed and were recorded by multiple-point potentiometers. The temperature as recorded at the midpoint was usually the maximum temperature measured along the thermocouple well. The auxiliary apparatus consisted chiefly of traps for collecting products and meters for measuring feed and exit gases and for regulating the flow of gases. Synthesis gas was scrubbed through a charcoal trap and passed downward through the catalyst bed.

Heavy oil, wax, and water in the gas-liquid mixture issuing from the bottom of the converter dropped into an air-cooled wax trap just below the converter. The vapors, after passage through air-cooled and ice-cooled traps, were led through a column of about 500 cc of active charcoal contained in a brass vessel (46 cm in length by 5 cm in diameter) and cooled to 0°C. The flow sheet, Figure 13, indicates the presence of two charcoal traps in the system; usually one was in use collecting products, while the other was being emptied of products. When iron cata-

[49] H. H. Storch, R. B. Anderson, L. J. E. Hofer, C. O. Hawk, H. C. Anderson, and N. Golumbic, *U. S. Bur. Mines Tech. Paper* 709 (1948), pp 73–88.

[50] *Annual Report of the Secretary of the Interior on the Synthetic Liquid Fuels Act*, year ended Dec. 31, 1947, pp 82 ff.

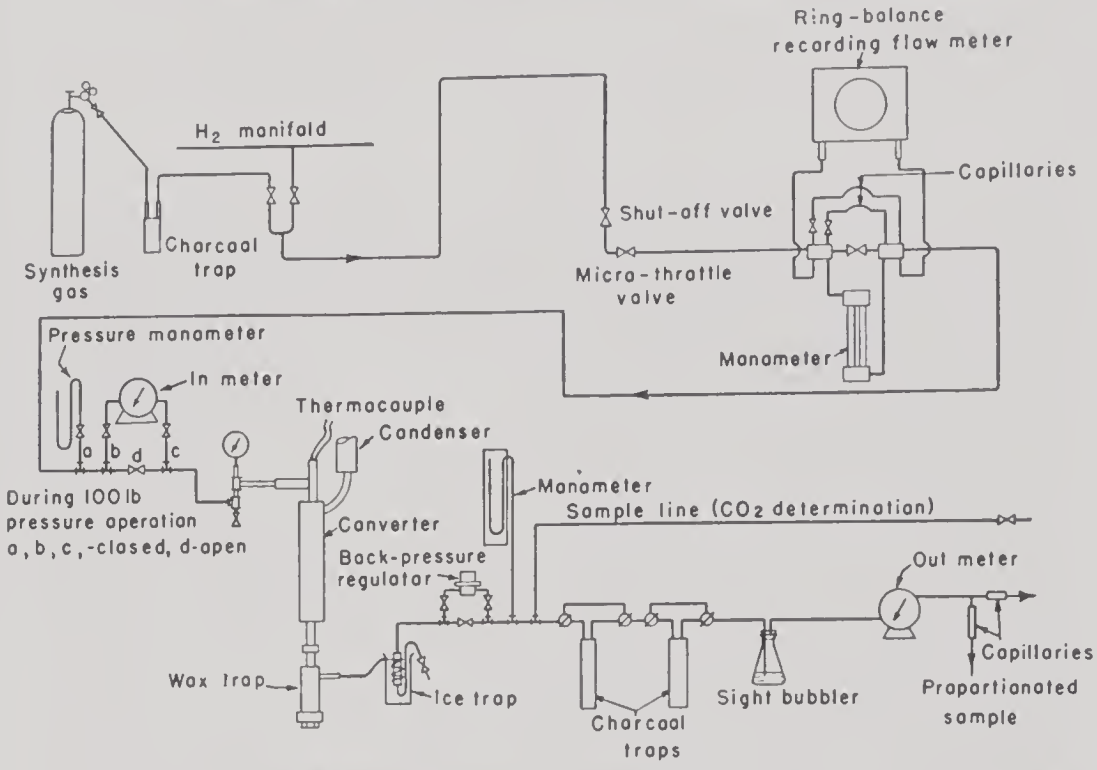


FIGURE 3–13. Flow diagram for catalyst tests. Reproduced from reference 49.

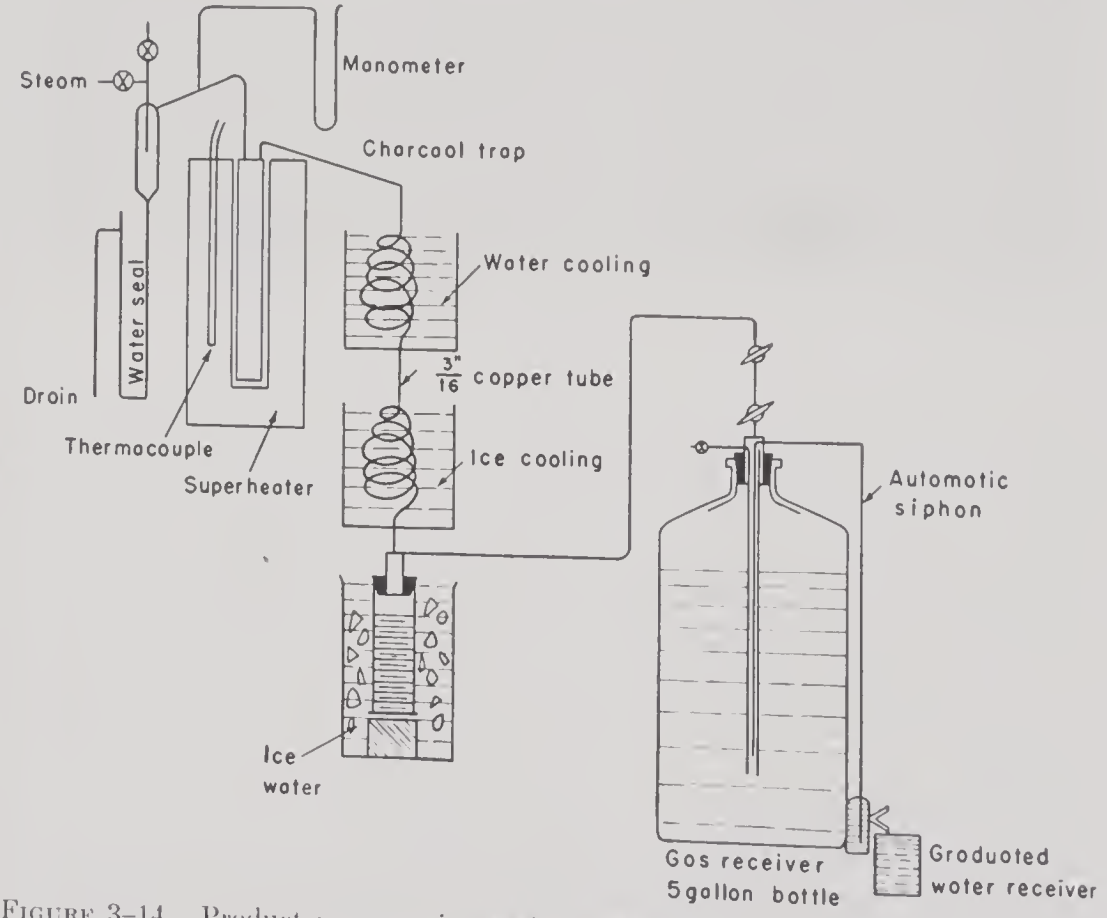


FIGURE 3–14. Product recovery in catalyst tests. Reproduced from reference 49.

lysts were tested, carbon dioxide was removed before the gas entered the charcoal adsorber. The continuously collected sample of the exit gases from the charcoal adsorber and a sample of vapors periodically recovered from the charcoal by steaming were analyzed in a mass spectrometer.

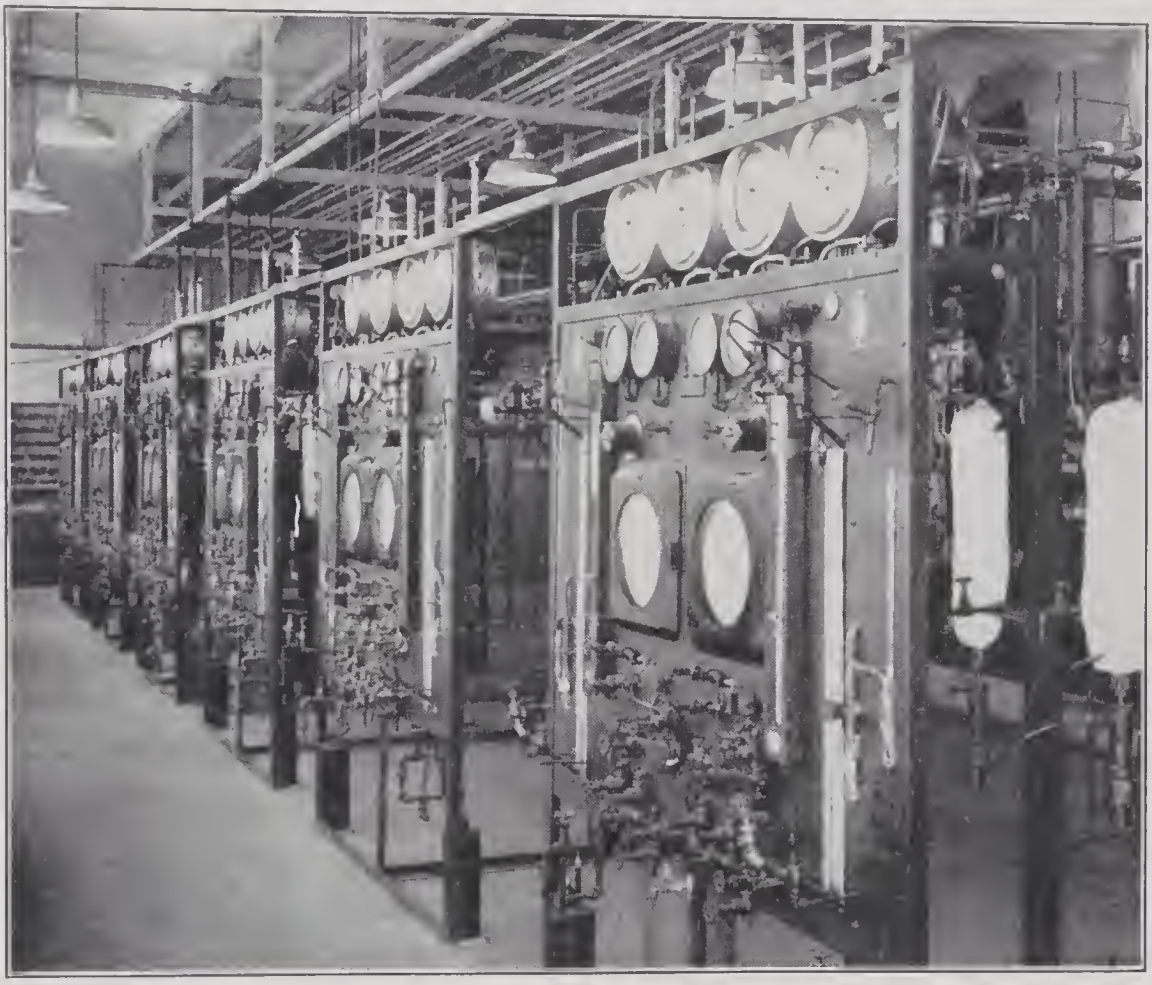


FIGURE 3–15. U. S. Bureau of Mines Fischer-Tropsch catalyst-testing units (*front view*). Reproduced from reference 50.

The liquid product recovered from the steaming of the charcoal was collected and weighed; this liquid product probably contained a very small quantity of dissolved C_2–C_4 hydrocarbons.

Synthesis gas was manufactured by passing natural gas, steam, and carbon dioxide in suitable proportions over a nickel catalyst at 1,000°C. For cobalt catalysts, $2H_2 + 1CO$ gas mixture was prepared, and for iron catalysts, $1H_2 + 1CO$. The synthesis gas contained approximately 0.5 per cent of inerts. The sulfur content of this gas was less than 0.5 grain per 1,000 cu ft.

At the U. S. Bureau of Mines, Co-ThO_2-MgO-kieselguhr catalysts were reduced in the reactor by heating to 400°C in nitrogen and then for 2 hr at 400°C in dry hydrogen flowing at a space velocity of 3,000. The yields from the 89-type catalysts varied from 50 to 100 g C_5+ hydro-

carbons per cu m synthesis gas charged, and the space-time-yields were in the range 5–12 kg per cu m catalyst space per hr. Some typical data are summarized in Table 12. The specific yields were obtained at a fixed contraction of 70 per cent; they would be about 50 per cent greater in a

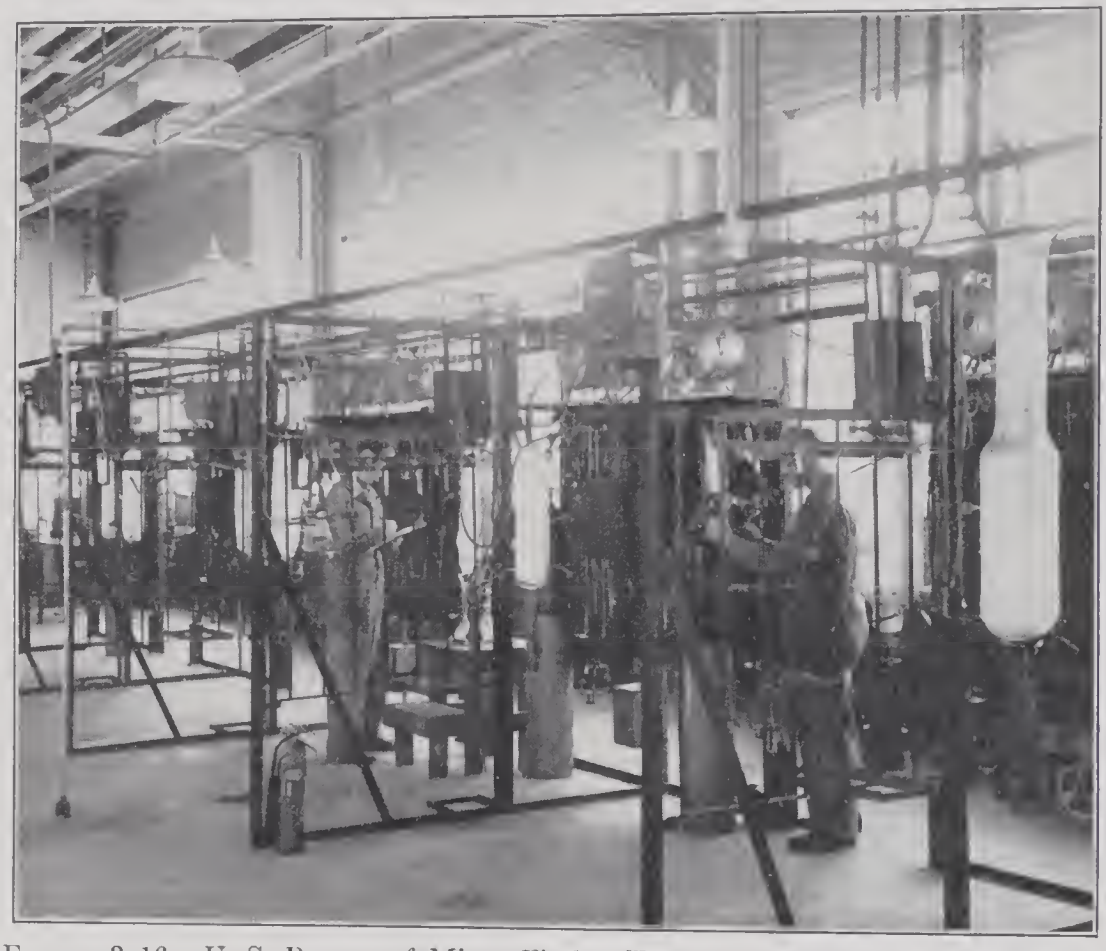


FIGURE 3–16. U. S. Bureau of Mines Fischer-Tropsch catalyst-testing units (*rear view*). Reproduced from reference 50.

multistage process. Catalyst 112A was somewhat less active than the good 89 catalysts and operated at a high average temperature of 195°C.

The data summarized in Table 12 were used to determine the reproducibility of the Co-ThO_2-MgO-kieselguhr catalysts during activity tests under similar conditions. In columns 2 and 3 are summarized data for two tests of granular catalyst 89K. The data of Table 12 were compared, using a statistical method developed by Student.[51] With this method the probability that two groups of data may be samples of the same "parent group" is estimated. The probability of finding differences of means greater than observed, on the basis of two samples taken from the same parent group, was computed. If this probability was less than

[51] Student, *Biometrika*, 6, 1, 1908; Yule and Kendall, *Introduction to the Theory of Statistics*, Charles Griffin & Co., London, 1937, p 442.

8 per cent, the samples were probably from different parent groups, and the difference was probably significant. For probabilities from 8 to 25 per cent the differences were regarded as possibly significant, and for probabilities greater than 25 per cent, differences were considered not

TABLE 12. TESTS OF Co-ThO_2-MgO-KIESELGUHR CATALYSTS AT ATMOSPHERIC PRESSURE OF $2H_2 + 1CO$ (U. S. BUREAU OF MINES)

1	2	3	4	5	6	7	8	9
Catalyst [a]	89K—G [b]	89K—G	89K—P	89Q—P	89O—P	112A—P [b]	89J—P	89J—G
Kieselguhr [c]	A	A	A	A	B–A	B	B	B
Total time, hr	1,045	1,040	1,070	1,100	1,060	1,120	1,075	545
Space velocity [d]	100	100	100	100	95	100	110	100
Average temperature, °C	186	188	176	182	181	195	186	194
Contraction, per cent [e]	74	74	73	69	70	70	72	63
Products, g per cu m feed gas								
CH_4	17.1	17.6	21.6	17.1	16.9	19.1	21.3	15.2
C_1–C_4	33.4	30.2	37.0	31.9	29.0	40.0	33.9	27.7
Average liquids [f]	97.0	89.5	90.8	91.8	95.9	85.8	102.2	85.4
Maximum liquids	115.1	105.0	102.4	102.7	109.8	92.4	118.4	95.0
H_2O	177.1	177.4	180.7	174.4	175.4	179.0	190.9	149.9
Liquids, weight per cent of total hydrocarbons	73.9	74.8	71.0	74.2	76.8	68.2	75.0	75.5
Space-time-yield [g]	9.7	8.9	9.1	9.2	9.2	8.6	11.5	8.3

[a] P = pellets; G = granules.

[b] Catalyst was inducted by temperature schedule. Synthesis gas was introduced at 150°C and the temperature increased to 175°C within an hour. After 48 hr, the temperature was increased to 180°C and after 24 additional hr to the temperature necessary to maintain 70–75 per cent contraction. All other catalysts were inducted by contraction schedule—introducing synthesis gas at 150°C and increasing temperature after 30 min to produce a contraction of 45–50 per cent, 175°C being the upper limit. After 48 hr, upper limit on the temperature was that required to produce a contraction of 45–50 per cent, or 180°C, and after 24 additional hr, the temperature was increased to give 70–75 per cent contraction. Tests showed that induction conditions had no significant effect upon catalyst activity.

[c] A = Portuguese; B = Filter-Cel; B—A = Filter-Cel acid-extracted.

[d] Volume of gas (STP) per volume of catalyst per hour.

[e] Per cent contraction = 100 (1 − flow out per flow in).

[f] Includes small amounts of dissolved wax and C_5 + hydrocarbons in gas from charcoal distillation.

[g] Kilograms of liquid hydrocarbons per cubic meter of catalyst per hour.

significant. Although slightly different induction procedures were used in these two tests, the differences between them were probably not significant, as shown in Table 13, rows 1 and 2.

Pelleted catalysts 89K and 89Q were prepared in an identical manner, upon the same kieselguhr. In the tests of these catalysts (columns 4 and 5 of Table 12), the means of the data showed greater differences than those of the tests of granular catalyst 89K. The statistical test (Table 13, rows 3 and 4) showed significant differences in temperatures and amounts of carbon dioxide, methane, and C_1–C_4 hydrocarbons. Part of these differences may be attributed to the higher density of catalyst 89K. Pelleted catalysts 89K and 89O (columns 4 and 6 of Table 12)

were precipitated in an identical manner upon similar kieselguhrs. The statistical comparison of these catalysts, shown in rows 5 and 6 of Table 13, indicated significant differences in temperatures and amounts of carbon dioxide, methane, and C_1–C_4 hydrocarbons. Comparison of

TABLE 13. STATISTICAL COMPARISON OF CATALYST-TESTING DATA BY METHOD OF STUDENT

(Averages of about 1,100 hr of operation.)

Duration of Test, hr	Catalyst and Form [a]	Weight of Catalyst, g	Contraction, per cent [b]	Temperature, °C	Grams per Cubic Meter				Liquid Hydrocarbons
					CO_2	H_2O	CH_4	C_1–C_4	
1,045	89K—G	16.9	74.4	186.0 [c]	8.3	177.1	17.1	33.4	97.0 [c]
1,040	89K—G	16.0	73.5	187.9 [c]	8.0	177.4	17.6	30.2	89.5 [c]
1,070	89K—P	38.8	72.7	176.1 [d]	12.7 [d]	180.7 [c]	21.6 [c]	37.0 [c]	90.8
1,100	89Q—P	34.2	68.8	182.0 [d]	6.1 [d]	174.4 [c]	17.1 [c]	31.9 [c]	91.8
1,070	89K—P	38.8	72.7	176.1 [d]	12.7 [d]	180.7	21.6 [c]	37.0 [d]	90.8
1,060	89O—P	28.5	69.6	181.0 [d]	5.6 [d]	175.4	16.9 [c]	29.0 [d]	95.9
1,040	89K—G	16.0	73.5	187.9 [d]	8.0 [d]	177.4	17.6 [c]	30.2 [d]	89.5
1,070	89K—P	38.8	72.7	176.1 [d]	12.7 [d]	180.7	21.6 [c]	37.0 [d]	90.8
545	89J—G	11.0	63.0	194.0 [d]	4.4 [d]	149.9	15.2 [d]	27.7 [c]	85.4
1,075	89J—P	30.5	72.0	186.0 [d]	8.0 [d]	190.9	21.3 [d]	33.9 [c]	102.2

[a] G = granules; P = pellets.
[b] Per cent contraction = 100 (1 − flow out per flow in).
[c] Difference possibly significant.
[d] Difference probably significant.

pelleted catalyst 112A with pelleted 89K and 89J (columns 4, 7, and 8 of Table 12) showed that 112A was operated at a significantly high temperature of 195°C. All three catalysts were precipitated upon similar kieselguhrs, but differed with respect to the source of magnesium used in preparation. Finely divided MgO was used in 89K and 89J; in 112A, the magnesia was precipitated from magnesium nitrate before being added to the cobalt-thorium nitrates.

EFFECT OF SHAPE OF CATALYST

The development of the Fischer-Tropsch synthesis from the laboratory to full-scale operation gave rise to an important problem which was concerned with the shape in which the catalyst was prepared to prevent it from disintegrating in the converter. Ruhrchemie studies on the

methods of producing granules suitable for commercial-size converters were mentioned previously in this chapter. U. S. Bureau of Mines laboratory studies of the effect of the shape of the cobalt catalyst upon its activity are discussed below.

In the statistical comparison of atmospheric-pressure tests with granules (6–10 mesh) and pellets (3.2- by 1.6-mm cylinders) of catalysts S9K and S9J, respectively, significant differences were found in temperature (Figure 17), carbon dioxide, methane, and C_1–C_4 hydrocarbons

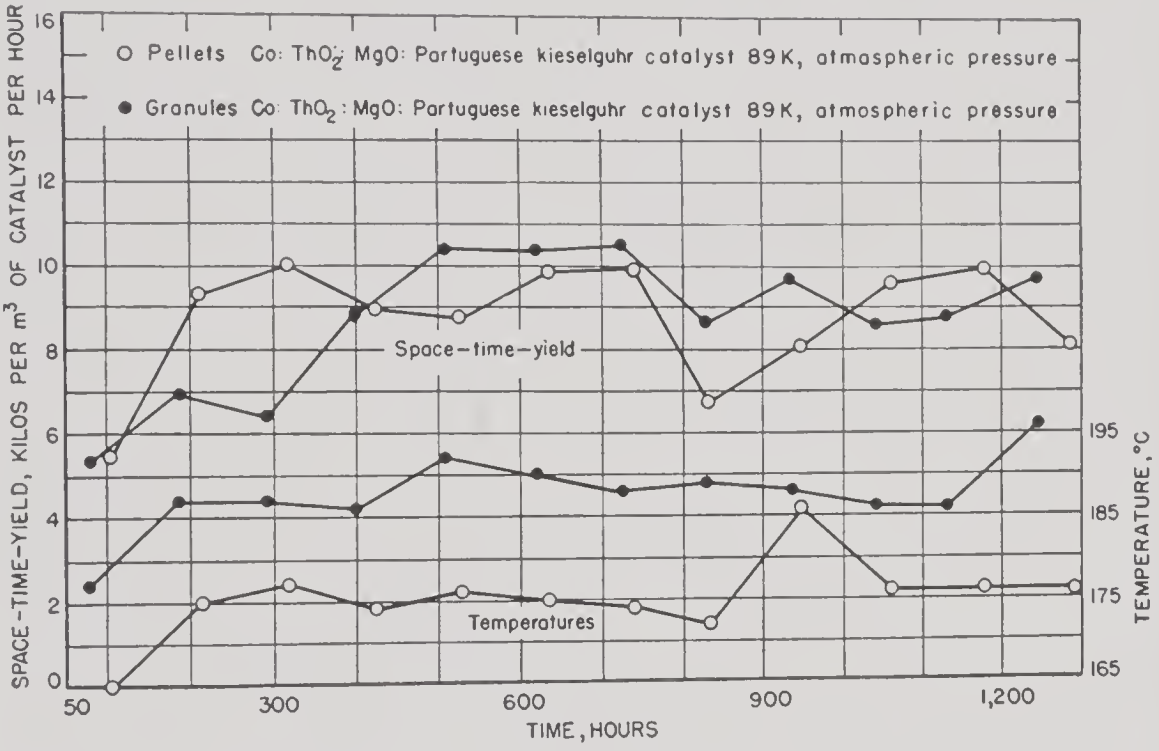


FIGURE 3–17. Relative activities of pellets (about 0.8 bulk density) and granules (about 0.3 bulk density). Reproduced from reference 49.

(rows 7–8 and 9–10 of Table 13). The greater amounts of carbon dioxide and light hydrocarbons produced by the pelleted catalysts resulted from the higher density of the pellets and not from differences in temperature, since at the lower temperatures at which the pellets were operated, smaller quantities of these products could be expected. The temperature difference was due to the greater weight of the pelleted catalysts, and it disappeared when the granular and pelleted forms were compared at equal flow of synthesis gas per gram of catalyst (Figure 18). The space-time-yields (kilograms per cubic meter of catalyst per hour) were not significantly different for the two forms, as shown in Figure 17. Pellets of two different sizes, 3.2 mm by 3.2 mm and 3.2 mm by 6.4 mm, of 100Co:18ThO_2:100 kieselguhr catalyst 108B, when tested at 7.8 atm, showed significant differences in activity. The data in Table 14 show that the larger, more dense pellets produced a larger fraction of gaseous hy-

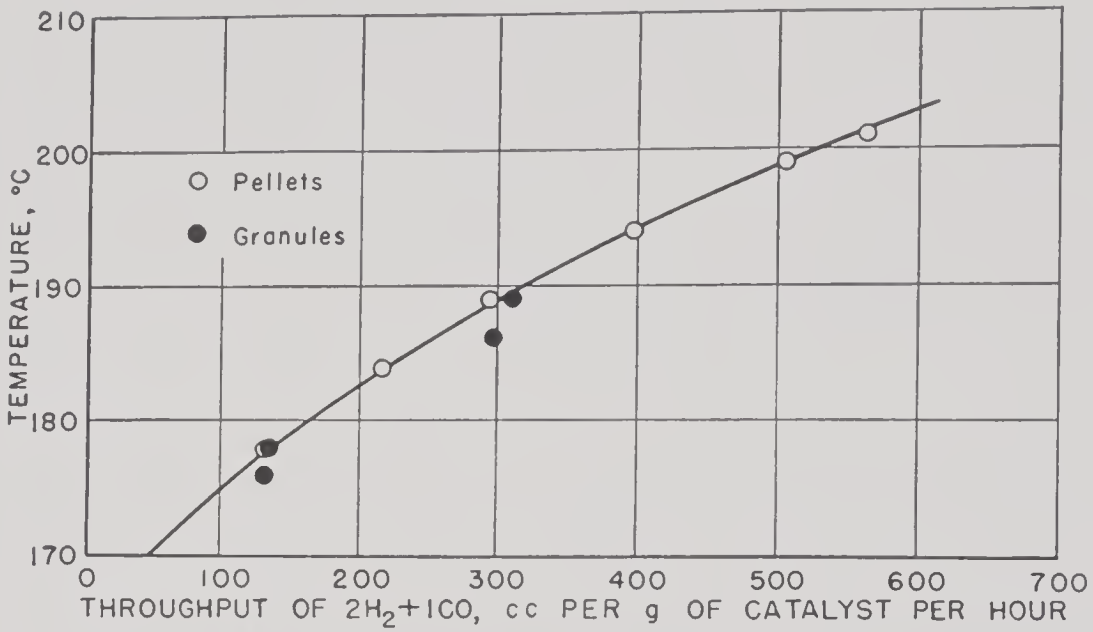


FIGURE 3–18. Variation of temperature with flow of $2H_2 + 1CO$, at constant contraction. Reproduced from reference 49.

drocarbons and less oil than the smaller pellets.[52] The larger pellets were operated at a higher temperature, even though a greater weight of catalyst was used, probably because their surface was less accessible than that of the smaller pellets.

It was observed [53] that, when granules were pelleted, the surface area was decreased by 10–20 per cent. For example, when 3.2-mm-length

TABLE 14. EFFECT OF SIZE AND DENSITY OF PELLETS OF Co-ThO_2-KIESELGUHR CATALYST 108B IN MEDIUM-PRESSURE SYNTHESIS [a]

Size of Pellets, mm		Mercury Density, [b] g per cc	Catalyst Charge, g	Av Temperature of Test, °C	Contraction, per cent	Hydrocarbons, g per cu m [c]			Distribution of Products, weight per cent	
Length	Diameter					CH_4	C_1–C_4	C_5+	CH_4	C_5+
3.2	3.2	1.13	36.8	187	71.6	24.9	43.8	81.5	19.9	65.1
6.4	3.2	1.51	44.9	191	71.4	33.6	56.5	73.6	25.8	56.6

[a] Tests at space velocity of 100. Methods of reduction and induction were the same.
[b] Densities determined with mercury at atmospheric pressure.
[c] Grams per cubic meter of synthesis gas.

[52] R. B. Anderson, W. K. Hall, A. Krieg, and B. Seligman, *J. Am. Chem. Soc.*, **71**, 183–8 (1949).

[53] R. B. Anderson, W. K. Hall, H. Hewlett, and B. Seligman, *ibid.*, **69**, 3,114–9 (1947).

by 3.2-mm-diameter pellets were made, the area of Co-ThO_2-kieselguhr catalyst 108B decreased from 84.1 to 71.6 sq m per g. When these pellets were broken into small pieces and then repelleted into dense cylinders 6.4 mm in length by 3.2 mm in diameter, the area was decreased further to 66.5 sq m per g. This decrease in area may have resulted from several causes. First, the graphite used as a die lubricant formed highly polished external surfaces on the pellets and may have blocked the entrance to closed-end pores. To test this, 3.2-mm-length by 3.2-mm-diameter pellets of catalyst 108B were made without graphite. The resistance of this material to pelleting was sufficient to stop the motor of the pelleting machine and necessitated operation by hand. The pellets made in this manner were soft and poorly formed. Their area was 77.2 sq m per g, which was greater than that of pellets containing graphite; however, the greater area may have been due to the fact that these pellets were poorly formed and not compressed as much as those containing graphite. The second and more plausible explanation is that some of the particles of the cobalt basic carbonate-promoter complex were pressed together so closely that nitrogen molecules used in the determination of surface area could not penetrate the spaces between them. In pelleting, considerable deformation of the catalyst occurred, since the volume occupied by a pelleted catalyst was one-half to one-third of the bulk volume of the kieselguhr it contained. This indicates that the pore volume (volume of pores with openings smaller than 5 microns in diameter) and void space (volume of pores with openings larger than 5 microns in diameter) of the kieselguhr were decreased. Possibly, the cobalt-promoter complex, which was present in the void-space volume of the kieselguhr in the granules, was forced into the pore volume of the kieselguhr during pelleting. After reduction, granular catalyst 89K had the same area as reduced pelleted catalyst 89K.[54] This is consistent with the second hypothesis, since reduction would cause enlargement of pores so that all the surface would be accessible to nitrogen molecules. A detailed discussion of the properties and function of the kieselguhr will be found in the following section.

THE CARRIER (KIESELGUHR) STUDIES

The carrier is important if the reaction is highly exothermic, as in the Fischer-Tropsch synthesis. The heat produced by a dense, unsupported catalyst may exceed the capacity of the reactor to remove the heat of reaction, and the catalyst may be quickly destroyed. This was possibly the reason for the great improvement in the life of cobalt and nickel Fischer-Tropsch catalysts when kieselguhr was introduced into the cata-

[54] R. B. Anderson, W. K. Hall, and L. J. E. Hofer, *ibid.*, **70**, 2,465–72 (1948).

lyst. The part played by kieselguhr was believed to consist principally in establishing and maintaining the porosity of the individual granules. The following discussion shows that the nature of the kieselguhr influences the yields and life of the catalyst. However, the distribution of products appears to be independent of the type of kieselguhr and dependent chiefly upon the density of the catalyst. The latter property is directly dependent upon the quantity of kieselguhr present in the catalyst and is influenced also by the density of the carrier.

Properties of Kieselguhrs

Kieselguhrs are composed chiefly of diatoms. They may be of marine or fresh-water origin and they are always composed of hydrous amorphous silica and small amounts of alumina, iron oxide, and traces of other oxide impurities. Kieselguhr particles exhibit a variety of interesting forms that reflect to some extent the source of the material. Kieselguhrs formed in swamps sometimes contain rather high percentages of carbonaceous material, which is usually removed by calcination. In preparing commercial kieselguhrs, the crude material is crushed and then separated into fractions of varying particle sizes by screening, settling in water, air separation, or combinations of these methods. Some commercial kieselguhrs are heat-treated (calcined) and alkali-heat-treated (flux-calcined) to produce varying degrees of sintering to improve their properties as filter aids, for example.

Fischer believed that kieselguhr was an unsatisfactory carrier because of its poor thermal conductivity, which resulted in inefficient removal of the heat of reaction. The results of tests made in 1933 with the Ni-Mn-Al catalyst deposited on other carrier materials are compared with kieselguhr in Table 15.[26] Filter-Cel, a natural California kieselguhr,

Table 15. Effect of Carrier on Catalyst Productivity

Carrier	Temperature, °C	Contraction, per cent	Yield, g per cu m [a]
Hyflo-Super-Cel [b]	194	60	77
Standard-Super-Cel [b]	194	68	87
Filter-Cel [b]	194	73	96
Calcium carbonate	200	38	36
Basic magnesium carbonate	200	17	19
No carrier	198	54	65
Stüttgart carrier	214	30	24
Diatomite granules	214	58	50
Kieselguhr S.11 and starch	198	75	77–98

[a] Grams C_5+ hydrocarbons per cubic meter $2H_2 + 1CO$.
[b] From Johns-Manville Corp., Berlin.

and the kieselguhr (S.11) ordinarily used by Fischer produced the best catalysts. Eleven years later, U. S. Bureau of Mines workers in the Synthetic Liquid Fuels Research and Development Branch obtained similar results, when they observed that Hyflo-Super-Cel consistently produced less active catalysts than Filter-Cel. Hyflo-Super-Cel was manufactured by treating Filter-Cel with a small amount of sodium carbonate and calcining at about 900°C. In the U. S. Bureau of Mines laboratory, it was of interest to determine which properties of a kieselguhr were critical in catalyst preparation and also to find a source of a suitable, commercially available American kieselguhr. The properties of more than a dozen American kieselguhrs were studied and compared with those of two kieselguhrs of foreign origin which had been reported to produce active catalysts.[55]

Chemical analyses. Several kieselguhrs were analyzed for aluminum, iron, phosphorus, titanium, calcium, and sulfur, and the weight loss on ignition was determined. The results of these analyses are given in Table 16, in which the percentages of these impurities as elements are reported.

The Johns-Manville samples gave almost identical analyses, indicating that they came from the same deposit. The nitric acid-extracted Filter-Cel showed a 50 per cent decrease in the iron and aluminum content. The low weight loss on ignition of this sample and Hyflo-Super-Cel resulted from previous calcination. Dicalite 911 had a somewhat higher iron content and ignition loss. The Shasta County kieselguhr had high aluminum and iron content and a high weight loss on ignition. This sample had not been subjected to any separating method and possibly contained more clay than the others. The ignition loss of the Portuguese and German kieselguhrs indicates that these samples probably were heated at about 650°–700°C to remove carbonaceous materials. The iron and aluminum content of the Portuguese sample about equaled that of the Johns-Manville samples; the aluminum content of the German kieselguhr was very low and the iron high. Only very small quantities of phosphorus, titanium, and calcium were present in all the samples.

X-ray diffraction studies. By means of x-ray diffraction patterns the crystalline phases of kieselguhrs were identified; the width or diffuseness of the diffraction lines indicated crystallite size. The reactivity of kieselguhrs—for example, solubility in solutions from which catalysts are precipitated—depends upon the crystalline phase, crystallite size, and impurities such as clay and crystalline quartz. All the natural kieselguhrs showed chiefly amorphous x-ray patterns. The

[55] R. B. Anderson, J. T. McCartney, W. K. Hall, and L. J. E. Hofer, *Ind. Eng. Chem.*, **39**, 1,618–28 (1947).

TABLE 16. ELEMENTS OTHER THAN SILICA IN KIESELGUHRS

Kieselguhr		Weight Loss on Ignition, per cent	Percentages Computed as Elements					
Name	Description		Al	Fe	P	Ti	Ca	S
Hyflo-Super-Cel [a]	Marine, Lompoc, Calif., deposit, flux-calcined, filter aid	0.33	1.90	0.87	0.07	0.12	0.19	0.03
Filter-Cel [a]	Marine, Lompoc, Calif., deposit, natural, filter aid	3.47	1.87	0.85	0.10	0.13	0.31	0.03
Filter-Cel [a] (acid-extracted)	[b]	0.60	0.9	0.49	[c]	[c]	[c]	[c]
Dicalite 911	Fresh-water, Terrebonne, Ore., natural	4.28	2.29	1.49	0.01	0.16	0.46	0.09
Shasta County	Fresh-water, Shasta County, Calif., natural [d]	6.42	4.88	2.24	0.02	0.28	0.49	0.31
Portuguese	Fresh-water, Portugal, probably heated [e]	1.58	2.06	0.87	0.006	0.08	0.03	0.05
German	Probably Rostguhr [f]	1.66	0.58	3.86	0.01	0.08	0.27	0.19

[a] Johns-Manville Sales Corp.

[b] Extracted in U. S. Bureau of Mines laboratory with hot nitric acid for 6 hr, filtered, dried at 120°C, and finally heated at 650°C for 2 hr.

[c] Not determined.

[d] This sample was a part of the sample "California 2a" mentioned by Skinner [K. G. Skinner, A. A. Dammann, R. E. Swift, G. B. Eyerly, and C. R. Shuck, *U. S. Bur. Mines Bull.* 460 (1944), 87 pp]. In 1940, there was no commercial source of this material.

[e] This sample was secured from the British Fuel Research Station, which used it in cobalt Fischer-Tropsch catalysts.

[f] This sample was taken from the Ruhrchemie A.G. Sterkrade catalyst factory on Apr. 19, 1945, and was believed to be a sample of the German Rostguhr. It was probably mined in a fresh-water deposit near Hannover and calcined to 700°C to remove carbonaceous material.

Portuguese kieselguhr, despite its low water content, showed no crystallization, such as might be expected after calcination. X-ray diffraction patterns of various kieselguhrs and samples of cristobalite and quartz are shown in Figure 19, and these patterns are described in Table 17. Slight differences among these kieselguhrs occurred with respect to the quantity of crystalline matter; for example, a number of faint lines occurred in the Filter-Cel patterns, some of which disappeared on acid extraction. The remaining lines seemed to be those of quartz. The pattern of the Portuguese kieselguhr, as far as the faint lines were concerned, was very similar to the acid-extracted Filter-Cel. The pattern of the Shasta County kieselguhr contained faint lines which could not be attributed to quartz or any other crystalline silica. The large amount of impurities (8.0 per cent as compared with 2.9 per cent for Filter-Cel and 1.4 per cent for acid-extracted Filter-Cel) suggested that the strange lines were due to crystalline impurities. The other amorphous kiesel-

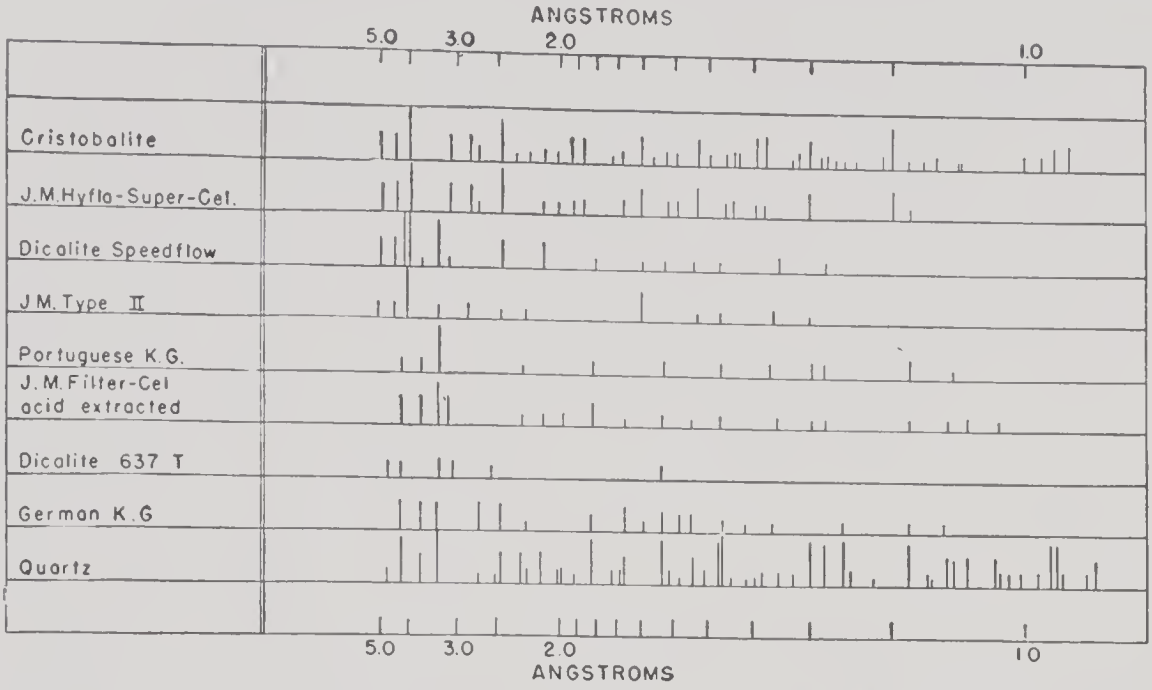


FIGURE 3–19. X-ray diffraction data for kieselguhrs, quartz, and cristobalite. Reproduced by permission from reference 55.

TABLE 17. X-RAY DIFFRACTION DATA ON KIESELGUHRS

Name	Description	Diffuseness	Phase
Johns-Manville			
JM I [a]	Marine, Lompoc, Calif., flux-calcined	A	Cristobalite
II [a]	Marine, Lompoc, Calif., calcined	C	Cristobalite
III [a]	Marine, Lompoc, Calif., natural	X	Amorphous
IV [a]	Marine, Lompoc, Calif., natural	X	Amorphous
Filter-Cel	Marine, Lompoc, Calif., natural	C⁻	Amorphous, quartz, unknown
Filter-Cel (acid-extracted)	.....	C⁻	Amorphous, quartz
Hyflo-Super-Cel	Marine, Lompoc, Calif., flux-calcined	A	Cristobalite
Dicalite			
Speed flow	Probably marine, Lompoc, Calif., flux-calcined, filter aid	B	Cristobalite, quartz
637T	Fresh-water, Nevada, natural	X	Amorphous
658T	Fresh-water, Washington, natural	X	Amorphous
SA5	Fresh-water, Nevada, natural	X	Amorphous
911	Fresh-water, Terrebonne, Ore., natural	X	Amorphous
Grade 1	Fresh-water, Terrebonne, Ore., natural	X	Amorphous
PS	Probably marine, Lompoc, Calif., flux-calcined, filter aid	C⁻	Cristobalite
Shasta County	Fresh-water, Shasta County, Calif., natural	C⁻	Amorphous, unknown
Portuguese	Fresh-water, Portugal, probably heated	C⁻	Amorphous, quartz
German	Probably Rostguhr	C	Quartz

[a] Catalyst supports.

A. Sharp.
B. Somewhat diffuse.
C. Diffuse.
C⁻. Diffuse to the point where phases are difficult to ascertain.
X. Amorphous.

guhrs gave very few faint lines. The x-ray diffraction analysis of the heat-treated silicas showed sharper patterns in every case.

The seven crystalline forms of silica, classified into a quartz series, a tridymite series, and a cristobalite series, and their interrelationships, are shown in Figure 20.[56] All the flux-calcined kieselguhrs and Johns-

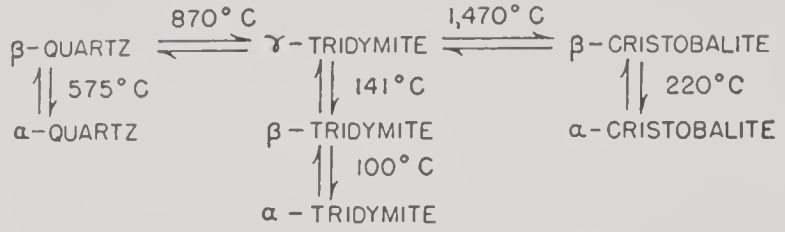


FIGURE 3–20. Transitions of silica. Constructed from data in reference 56.

Manville II, which was calcined at a high temperature, contained cristobalite. In addition, Dicalite Speedflow contained α-quartz, indicating incomplete conversion from quartz to cristobalite. The sharpness of the lines of German kieselguhr probably resulted from heating, but no indication of the presence of cristobalite could be found. Therefore, 870°C probably was not exceeded during heating. The Portuguese kieselguhr also contained quartz, but no cristobalite.

Surface areas, pore volumes, and electron micrographs. A reasonably good picture of the geometry of kieselguhr particles can be obtained from electron micrograph, pore volume,[57] and surface area studies.[53, 58] The procedures used to determine these properties are discussed in Chapter 2, pp 45–72. These data are significant, since the pore structure and density of catalysts depend at least to some extent on the properties of the kieselguhr used as carrier.

Surface areas of kieselguhrs, as determined by nitrogen adsorption isotherms at −195°C, varied from 15 to 37 sq m per g for natural materials, while calcined and flux-calcined samples had areas from 2 to 6 sq m per g. Surface areas, together with pore volume data obtained from helium and mercury densities, are given in Table 18.[55] These data are computed per gram of kieselguhr after evacuation at 100°C. The adsorption isotherms were of the S-type (type II of Brunauer's classification [59]; see Chapter 2), which would be expected for a system of pores of which the average size is larger than about 1,000 Å in diameter.

[56] R. Fricke and G. F. Hüttig, *Hydroxyde und Oxydhydrate, Handbuch der allgemeine Chemie*, Adademische Verlagsgesellschaft, Leipzig, 1937.

[57] W. R. Smith and R. P. Rossman, *Ind. Eng. Chem.*, **35**, 972–6 (1943).

[58] S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309–19 (1938).

[59] S. Brunauer, L. S. Deming, W. E. Deming, and E. Teller, *J. Am. Chem. Soc.*, **62**, 1,723–32 (1940); S. Brunauer, *Adsorption of Gases and Vapors*, Princeton University Press, 1943, p 150.

TABLE 18. SURFACE AREAS AND PORE VOLUMES OF KIESELGUHRS

Origin of Kieselguhr	Surface Area, sq m per g	Bulk Density, g per cc	Hg Density, g per cc	He Density, g per cc	Void Space, [a] cc per g	Pore [a] Volume, cc per g	Av [b] Pore Diameter, microns
Johns-Manville							
Filter-Cel	22.8	0.149	0.299	2.19	3.32	2.81	0.51
Filter-Cel (acid-extracted)	20.8	0.17	.....	....	....	....	....
Snow Floss [c]	19.4	0.186	0.343	2.33	2.46	2.48	0.52
Hyflo-Super-Cel	1.9	0.22	0.361	2.27	1.77	2.33	4.9
JM I	3.2	0.26	0.381	2.43	1.22	2.21	2.8
II	5.5	0.20	0.346	2.24	2.12	2.46	1.8
III	19.2	0.174	0.323	2.35	2.64	2.67	0.56
IV	12.4	0.228	0.406	2.22	1.92	2.01	0.66
Dicalite							
911	29.7	0.245	0.373	2.25	1.41	2.29	0.31
Grade 1	20.3	0.179	0.348	2.35	2.71	2.44	0.49
SA 5	37.7	0.203	0.372	2.05	2.23	2.20	0.24
637T	34.2	0.196	0.369	[d]	2.39	2.28	0.28
658T	25.4	0.215	0.335	2.20	1.67	2.55	0.40
Speedflow	3.5	0.214	0.372	2.34	1.94	2.26	2.6
PS	3.2	0.245	0.372	[d]	1.39	2.26	3.0
Shasta County	33.6	0.35	0.425	2.39	0.51	1.92	0.23
Portuguese	17.5	0.345	0.508	2.36	0.90	1.54	0.40
German	14.9	0.137	0.272	2.29	3.63	3.24	0.87

[a] Void space is volume of pores with openings larger than 5 microns in diameter (pores filled by mercury at atmospheric pressure) and is defined as difference of the reciprocals of the bulk and mercury densities. Pore volume is volume of pores with openings smaller than 5 microns (pores not filled by mercury at atmospheric pressure) and is defined as the difference of the reciprocals of the mercury and helium densities.

[b] Average pore diameter computed by $d = \frac{4 \times \text{pore volume}}{\text{surface area}}$.

[c] Marine, Lompoc, Calif., deposit, natural kieselguhr characterized by a very small particle size, filter aid.

[d] Not determined. Assumed to be 2.3 for pore volume estimation.

Isotherms of Shasta County, Filter-Cel, and Hyflo-Super-Cel kieselguhrs are given to fairly high relative pressures in Figure 21. Desorption points determined on the Shasta County and Filter-Cel kieselguhrs showed definite hysteresis, indicating the presence of some pores of diameters in the range 15–100 Å. If most of the area, A, is contributed by the surface of pores smaller than 5 microns in diameter, it is possible to calculate an average pore diameter, d, on the basis of cylindrical open-end pores by the equation, $d = 4V/A$, where V is the pore volume and A the surface area.[60] These diameters are given in the last column of Table 18.

[60] P. H. Emmett and T. W. DeWitt, *J. Am. Chem. Soc.*, **65**, 1,353–62 (1943).

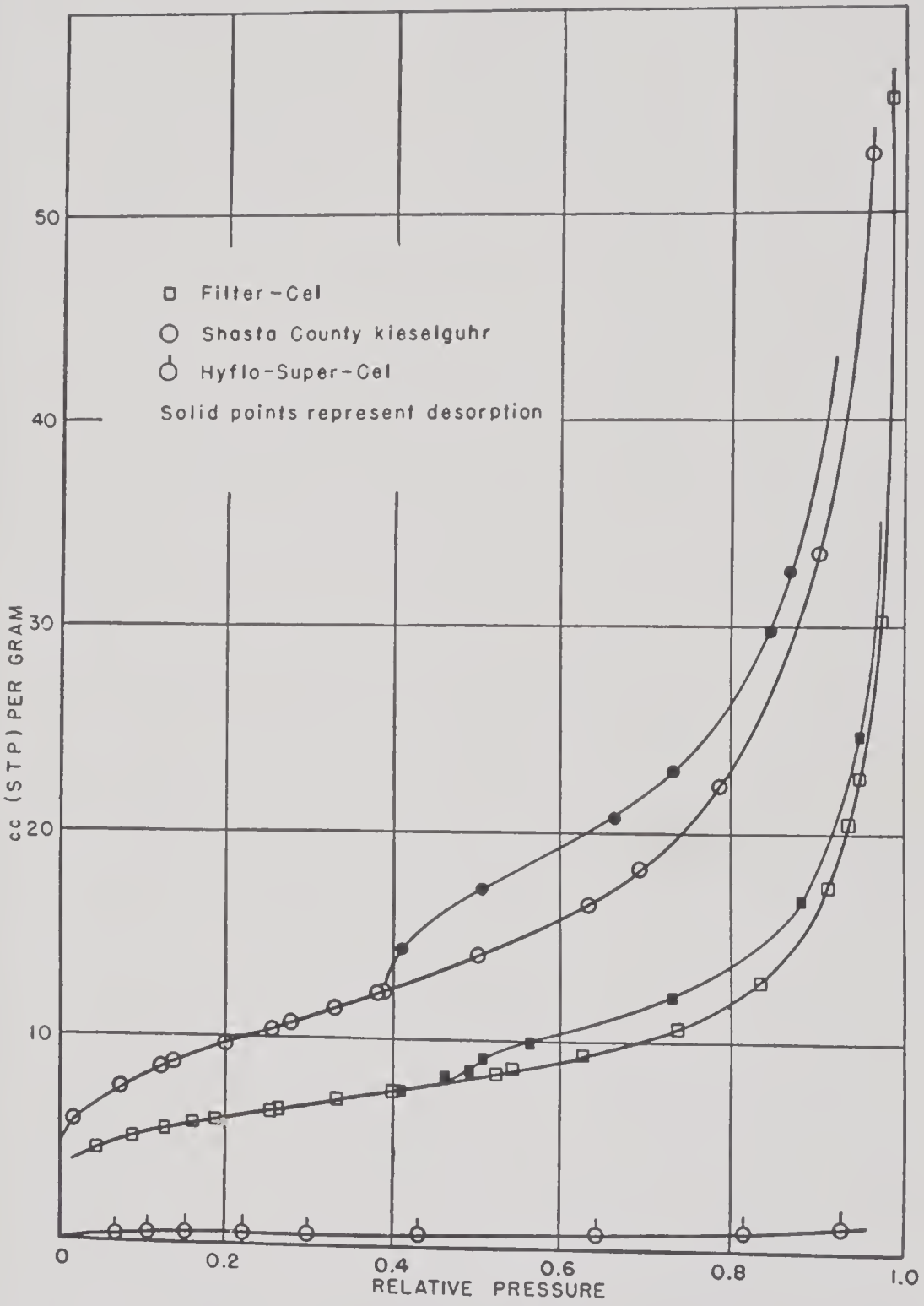


FIGURE 3–21. Adsorption of nitrogen on kieselguhrs at −195°C. Reproduced by permission from reference 55.

The electron micrographs at magnification of 2,000 of the Johns-Manville samples showed particles with a "rod and perforated plate" structure, the perforated plates probably being fragments of larger discs. This structure appeared to be characteristic of the marine deposit at Lompoc, Calif. The micrographs of calcined kieselguhrs showed loss in fine structure, the flux-calcined materials, JM I and Hyflo-Super-Cel, being more sintered than calcined JM II. The dicalite samples, obtained from several different deposits, had several characteristic forms, including rods, perforated discs, elliptical particles, and fine structure. The surface areas and pore volumes were in qualitative agreement with the micrographs.

The German kieselguhr had nearly perfect diatoms. The most prominent forms were discs and perforated rod or ladder-like structures. Because of the large proportion of elongated forms, the bulk density was low. The surface area was lower than anticipated from the apparent fine structure; this was probably due to the calcination at about 650°–700°C. A sample of kieselguhr obtained by extraction with hot nitric acid of a German cobalt Fischer-Tropsch catalyst was similar to the previous sample.

A large portion of the diatoms of the Portuguese fresh-water kieselguhr was broken into very small fragments of about 1 by 2 microns. Some particles of circular cross section about 5 microns in diameter were found. Some of the unbroken diatoms of this sample were similar to those of the German kieselguhr. It is possible that this sample had been heated at about 650°–700°C, for its surface area was lower than those of most of the fresh-water kieselguhrs. The fact that this sample was considerably broken was reflected in the high bulk and mercury densities of this material.

Micrographs of natural kieselguhrs at magnifications of 20,000 showed considerable fine structure not apparent at the lower magnification. The fine structure was of two types: small holes within larger holes, and fine structure apparent in thin pieces and at the edges of thick pieces. These micrographs showed pores as small as can be detected, about 100 Å. Although this fine structure was not apparent in the majority of the pieces of natural kieselguhr, it was found frequently. Calcined and flux-calcined kieselguhrs at magnifications of 20,000 showed significantly less fine structure than natural samples. In micrographs of flux-calcined samples, Hyflo-Super-Cel and JM I, there was no evidence of fine structure. The sample appeared sintered, as indicated by drop-shaped portions and smooth outlines of all particles. Some larger pores were eroded and enlarged until they merged with adjacent pores and all small pores

had disappeared. Speedflow and PS filler showed more fine structure, and the extent of sintering and erosion was smaller. Calcined sample JM II showed slightly more structure than Speedflow or PS filler.

German Kieselguhr

In all the small-scale tests made after 1933 at the Kaiser Wilhelm Institut für Kohlenforschung and at Ruhrchemie, kieselguhr S.11, mined in a fresh-water deposit near Hannover, was used. However, it was not available in sufficient quantities for commercial-scale preparations and a substitute material was sought. The only treatment given kieselguhr S.11 was screening, because it occurred at the top of the deposit and contained little organic matter or other impurities, such as iron and calcium. Iron was thought to increase the production of methane and carbon dioxide [29] during synthesis, the effect of soluble iron being somewhat greater than that of insoluble iron. Calcium was believed to exert a deleterious effect during precipitation of the catalyst. The type of diatom in the kieselguhr was thought to be unimportant, and no correlation was found between suitability as a catalyst carrier and surface area, as measured by adsorption of dyes. A low content of sand, measured by sedimentation analysis, was specified, because sandy kieselguhr produced a soft catalyst. Table 19 summarizes typical data on the physical and chemical properties of kieselguhrs, obtained by Ruhrchemie [61] in 1937 when various kieselguhrs were being tested to find a substitute for S.11. The first four kieselguhrs shown in the table were mined in the same region as S.11 and were calcined at 1,000°C; the next two, 10 SO and 12 SO, were untreated; and the last one was S.120. Table 20 shows the results of synthesis tests with catalysts containing these kieselguhrs. As a result of many tests of this type, it was concluded that the calcined kieselguhrs were more suitable than the untreated ones.

Kieselguhr S.120, which was selected to replace S.11, was prepared by heating at 1,000°C a mixture of several kieselguhrs, including I–IV of Table 19. It was calcined in order to volatilize some of the impurities (S, Cl) and convert others into insoluble silicates. This Gluhguhr (German spelling "Glühgur") had the great advantage that its bulk density was constant from batch to batch, at 120 g per l, and it was therefore known as kieselguhr S.120.[35] Table 21 shows the chemical analysis of S.120 and includes that of S.11 for comparison. A Ruhrchemie chemist was employed at the kieselguhr mines to supervise the mixing of the various kieselguhrs and calcination of the mixture, so that

[61] F.I.A.T. Reel K21, Frames 1,070–5.

TABLE 19. PROPERTIES OF RUHRCHEMIE KIESELGUHR

Kieselguhr No.	Physical Properties							Solubility								pH
	Microscopic Results	Abrasion Resistance, per cent [a]	Sand, per cent [b]	Filter No., sec per 100 cc [c]	Bulk Density, g per l [d]	Absorption of Water, per cent [e]	Loss at 1,000°C, [f] per cent	In 25 Per Cent HNO_3, per cent				In H_2O, per cent				
								Fe	Al	Ca	SO_4	Ca	Cl	SO_4		
I	Many long rods, few perforated discs	13.8	1.9	328	150	270	0.05	0.71	0.29	0.16	....	0.02	0.01	....		6.1
II	Long rods, few discs	17.5	1.05	348	131	295	0.1	0.50	0.12	0.05	Trace	0.01	0.01	0.01		6.3
III	Few rods, many discs	3.4	0.5	660	145	275	0.2	3.02	0.11	0.11	Trace	0.03	0.01	0.02		5.9
IV	Few rods, some discs	4.6	0.9	1.280	142	290	0.5	3.17	0.13	0.20	....	0.02	0.01	....		6.1
10 SO	No discs, many rods and round forms	....	....	1.620	151	330	2.7	1.49	0.50	0.44	0.80	0.23	Trace	0.55		5.6
12 SO	Very long rods, no discs, some round forms	....	....	1,640	123	330	3.0	1.24	0.27	0.23	0.45		Traces			
S.120	Many perforated discs, few rods	9.2	2.1	390	130	330	0.25	0.95	0.08	0.25	0.05	0.03	0.01	0.05		5.3

[a] Residue of 5-mm particles obtained after 10 g kieselguhr was subjected to a blast from a 3.5-mm nozzle for 8 min in the Schulz-Harkort apparatus.
[b] Schulz-Harkort test.
[c] Two grams kieselguhr slurried in 200 cc 30 per cent sugar solution at 90°C and filtered. Time, in seconds, required to collect 100 cc filtrate was measured.
[d] Kieselguhr dropped into graduate cylinder from a height of 50 100 cm and weight per unit volume measured.
[e] Water added to 20 g kieselguhr, with stirring, until the mixture could flow.
[f] Twenty grams kieselguhr was dried to constant weight at 120°C and calcined 1 hr at 1,000 1,050°C.

TABLE 20. ACTIVITY TESTS OF 100Co:15ThO_2:200 KIESELGUHR CATALYSTS, ON VARIOUS KIESELGUHRS, RUHRCHEMIE, NOVEMBER 1937 [a]

Kieselguhr No.	Catalyst No.	Synthesis Tests [b]											
		Average Contraction, per cent, after						Total Liquid Hydrocarbon, cc per cu m, after					
		100 hr	200 hr	300 hr	400 hr	500 hr	Av	100 hr	200 hr	300 hr	400 hr	500 hr	Av
I	523	72	70	69	66	62	68	..	135	132	117	111	124
	527	71	71	69	66	64	68	..	127	121	.	114	121
II	524	69	70	68	66	64	67	..	134	129	128	124	129
	528	71	70	67	67	63	68	..	112	123		109	115
III	525	68	66	67	67	64	66	..	121	130	124	116	123
	529	69	65	66	67	65	66	..	...	127	...	115	121
IV	526	69	66	68	67	64	67	..	118	130	124	114	122
	530	70	69	68	68	67	68	..	129	130	...	120	126
10 SO	481	63	60	..	..	..	62	..	...	...	...	...	...
	482	63	58	..	..	..	61	..	...	...	...	...	...
12 SO	515	65	61	59	63	..	62	..	120	117	122	...	120
	515	63	62	..	..	..	63	..	...	...	...	...	...

[a] Catalysts were reduced at 400°C, 2 hr, 300 l H_2-N_2 per hr.

[b] Synthesis tests were carried out at 185°C for 400–500 hr. Flow rate was 4 l synthesis gas per 4 g Co.

TABLE 21. CHEMICAL ANALYSIS OF GERMAN KIESELGUHR (PER CENT BY WEIGHT)

Constituent	S.120	S.11
SiO_2	94.7	93.3
Fe_2O_3	2.1	0.8
Al_2O_3	1.9	0.5
CaO	0.7	0.3
MgO	0.2	0.7
Loss on drying (110°C)	0.1	4.0
Loss on calcination (1,000°C)	0.1	8.0

the final product conformed to the specifications (Table 22) that had been adopted for Gluhguhr.[29] However, despite all precautions, catalysts prepared with Gluhguhr did not have the highest activity.

TABLE 22. SPECIFICATIONS FOR GERMAN KIESELGUHR

Property	Gluhguhr	Rostguhr
Bulk density, g per l	120–150	60–100
Sand content, per cent [a]	<2	<2
Acid-soluble constituents, per cent [b]		
Fe	1	1.7
Al	0.1	0.4
Ca	0.2	0.2
SO_4	0.4	0.6
Loss on heating at 1,000°–1,050°C for 1 hr, per cent	0.5	2.5

[a] Schulz-Harkort test.

[b] Values given must not be exceeded after boiling 1 part of kieselguhr for 1 hr with 5 parts of 25 per cent HNO_3.

In 1938, the demand for kieselguhr for catalyst manufacture was so great that the capacity of the calcination equipment at the Vereinigte Deutsche Kieselgurwerke, Hannover, was exceeded.[31] Further tests showed that heating the kieselguhr at about 600°–700°C produced a material more suitable for catalyst manufacture than Gluhguhr. This result indicated that calcination at 1,000°C, which produced considerable sintering, rather than the presence of impurities in the kieselguhr, had been the important factor in the production of unsuitable kieselguhrs. Subsequently, all kieselguhr was treated by roasting at 400°–700°C in a moving layer. The product, Rostguhr ("Röstgur") (Table 22), varied in bulk density from 60 to 100 g per l, so that varying proportions (180–200) were used during the manufacture of the catalyst in order to maintain a constant cobalt content of 80 g per l of unreduced catalyst granules. The use of Rostguhr also improved the mechanical strength of the catalyst granules (in addition to the improvement observed when magnesia was incorporated into the catalyst).[41] Kieselguhr fulfilling the conditions for the preparation of active catalysts gave rise to no difficulties in the recovery of the metals from used catalysts. The kieselguhr was not recovered; handling, such as passage through pumps, destroyed the diatomaceous structure and rendered the kieselguhr unsatisfactory for reuse in catalysts. Ample supplies of kieselguhr suitable for conversion to Rostguhr were available in Germany, and little work was done on kieselguhrs from other sources.

Effect of Kieselguhr on Catalyst Activity

U. S. Bureau of Mines tests summarized in Tables 23 and 24 showed the effect of the nature of the kieselguhr upon the activity of Co-ThO_2-MgO-kieselguhr catalysts. The data in columns 2, 3, and 4 of Table 23 showed that pelleted catalysts 89I, 89L, and 89H produced average liquid hydrocarbon yields of about 80 g per cu m of feed gas. These catalysts were precipitated on Hyflo-Super-Cel kieselguhr, which is a flux-calcined material. The natural kieselguhr from which Hyflo-Super-Cel was manufactured, Filter-Cel, and the natural kieselguhr of Portuguese origin produced significantly more active catalysts. Catalysts 89J and 89K (columns 7 and 15 of Table 23, respectively) produced an average of 97 g per cu m of feed gas, at much lower temperatures. The relative efficiencies of Hyflo-Super-Cel, Filter-Cel, and Portuguese kieselguhr as catalyst carriers are shown graphically in Figure 22, in which, for purposes of comparison, the space-time-yields and temperatures at a

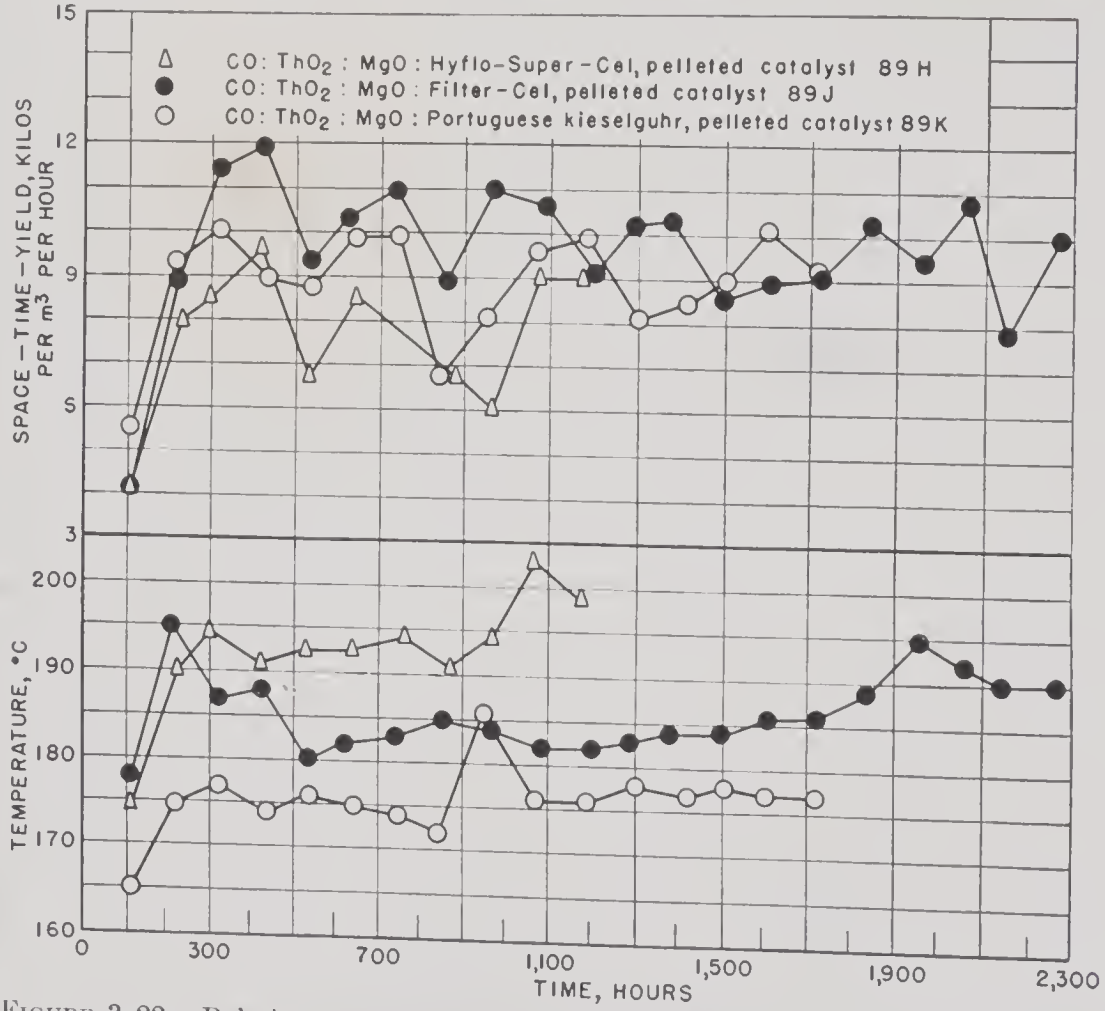


Figure 3–22. Relative efficiencies of Hyflo-Super-Cel, Filter-Cel, and Portuguese kieselguhr as catalyst carriers. Constructed from data in reference 20.

TABLE 23. EFFECT OF KIESELGUHR UPON ACTIVITY OF PELLETED Co-ThO_2-MgO-KIESELGUHR CATALYSTS AT ATMOSPHERIC PRESSURE WITH $2H_2 + 1CO$ SYNTHESIS GAS (U. S. BUREAU OF MINES)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Kieselguhr [a]	H				I	B	B—A	B—A	C	D	D—A	E	F	A	G
Catalyst	89I	89L	89H	89N [b]	89BB	89J	89O	89FF	89DD	89V	89GG	89Y	89Z	89K	89U
Total time, hr	1,059	1,201	1,063	508	1,071	1,075	1,060	1,030	1,030	1,150	1,155	1,145	1,120	1,070	1,150
SVH [c]	100	100	100	100	100	110	95.5	114	110	110	105	100	120	100	105
Average temperature, °C	190	192	194	193	185	186	181	183	189	187	183	179	187	176	189
Contraction, per cent [d]	67	72	63	68	71	72	70	69	70	71	70	72	71	73	71
Products, g per cu m [e]															
CH_4	20.3	13.4	20.3	19.5	20.2	21.3	16.9	19.3	18.4	22.2	23.6	21.5	16.3	21.6	17.7
C_1-C_4	35.3	33.6	35.9	37.4	37.1	33.9	29.0	36.3	35.0	37.9	40.1	38.0	28.1	37.0	32.5
Average liquids [f]	76.2	80.6	85.7	98.0	86.4	102.2	95.9	90.9	90.3	97.0	77.3	85.2	99.7	90.8	92.3
Maximum liquids	94.5	100.8	103.2	113.9	102.3	118.4	109.8	137.7	101.3	108.2	99.0	95.9	118.3	102.4	100.3
H_2O	142.9	159.1	160.3	179.9	174.9	190.9	175.4	171.8	177.2	183.5	182.1	175.4	192.5	180.7	173.8
Liquids, weight per cent of total hydrocarbons	68.4	70.6	70.4	72.4	70.0	75.0	76.8	71.5	72.0	71.8	65.4	69.1	78.0	71.0	74.0
Space-time-yield [g]	7.6	7.9	8.6	9.8	8.6	11.5	9.2	10.4	10.1	10.8	8.3	8.6	11.9	9.1	9.6

[a] A = Portuguese; B = Filter-Cel; B—A = Filter-Cel acid-extracted; C = Snow Floss; D = Dicalite 911; D—A = Dicalite 911 acid-extracted; E = Dicalite SA5; F = Dicalite 658T; G = German; H = Hyflo-Super-Cel (HSC); I = Johns-Manville II.

[b] Contained alkali-washed magnesia.

[c] Space velocity per hour. Volumes of gas (STP) per volume of catalyst per hour.

[d] Per cent contraction = 100 (1 — flow out per flow in).

[e] Grams per cubic meter of feed gas.

[f] Includes small amounts of dissolved wax and C_5 and higher hydrocarbons in gas from charcoal distillation.

[g] Kilograms of liquid hydrocarbons per cubic meter of catalyst per hour.

space velocity of 100 were estimated from the data of Table 23. The Hyflo-Super-Cel-containing catalyst operated at significantly higher temperatures and produced a space-time-yield about 2 kg per cu m of

TABLE 24. EFFECT OF KIESELGUHR ON ACTIVITY OF Co-ThO_2-MgO-KIESELGUHR CATALYSTS (U. S. BUREAU OF MINES)

Kieselguhr	Catalyst	Duration of Test, hr	Activity,[a] cc per g per hr	Surface Area of Kieselguhr, sq m per g	Weight Per Cent Extractable [b]				
					Al^{+3}	Fe^{+3}	Ca^{+2}	PO_4^{-3}	SO_4^{-2}
Flux-calcined									
HSC	89I	1,059	63.2	1.9	0.05	0.03	0.00	0.00	0.00
HSC	89L	1,201	52.4	1.9					
HSC	89H	1,063	48.7	1.9					
HSC	89N [c]	508	45.2	1.9					
Calcined									
Johns-Manville 11	89BB	1,071	88.3	5.5	0.17	0.04	0.00	0.13	0.09
Natural, marine									
FC	89J	1,075	127.4	22.2	1.23	0.75	0.12	0.09	0.11
FC-A [d]	89O	1,060	166.8	20.8	0.00	0.00	0.00	0.00	0.00
FC-A [e]	89FF	1,030	115.5	24.1	0.00	0.00	0.00	0.00	0.00
Snow Floss	89DD	1,030	86.6	19.1	0.80	0.70	0.28	0.15	0.12
Natural, fresh-water									
Dicalite 911	89V	1,150	92.7	29.3	1.41	1.14	0.35	0.00	0.26
Dicalite 911-A [e]	89GG	1,155	164.5	39.2	0.00	0.00	0.00	0.00	0.00
Dicalite SA5	89Y	1,145	110.7	37.3	....	....	....	....	....
Dicalite 658T	89Z	1,120	94.6	25.2	0.76	1.77	0.14	0.00	0.23
Portuguese	89K	1,070	166.3	17.5	1.61	0.65	0.00	0.00	0.11
German	89U	1,150	79.6	14.9	0.43	1.49	0.02	0.00	0.56

[a] Computed activity at 185°C, expressed as cubic centimeters (STP) of $2H_2 + 1CO$ gas converted per gram of unreduced catalyst per hour.

[b] By heating in 8 *N* nitric acid for 2 hr.

[c] Alkali-washed magnesia.

[d] Kieselguhr was extracted with hot nitric acid for 6 hr, washed, dried, and heated at 650°C for 2 hr. The extraction decreased the percentages of aluminum and iron by about 50 per cent. (See reference 20.)

[e] Kieselguhr was extracted with hydrochloric-nitric acid solution (1 volume each of concentrated acids and 2 volumes of water) for 16 hr at room temperature. Then it was washed and dried at 400°C.

catalyst per hr lower than the catalysts prepared with Filter-Cel or Portuguese kieselguhrs. Catalyst 89H produced significantly more carbon dioxide than 89J; this result was consistent with the smaller pore volume of 89H. The catalyst made with Filter-Cel (89J) gave slightly higher space-time-yields but also operated at a higher temperature than the catalyst containing the Portuguese kieselguhr (89K). The difference

in operating temperature was partly the result of the greater weight of catalyst 89K. The other tests reported in Table 23 confirmed the observation that flux-calcined and calcined kieselguhrs in general produced less active catalysts than the natural or untreated materials. In order to make a reliable comparison of the tests of the various catalysts, values were computed expressing activity as cubic centimeters (STP) of $2H_2 + 1CO$ gas converted per gram of unreduced catalyst per hour, at 185°C. Table 24 [62] shows clearly that catalysts containing flux-calcined Hyflo-Super-Cel kieselguhr were the least active. The preparation containing calcined Johns-Manville II was considerably more active; however, its activity was lower than that of preparations containing natural kieselguhrs. The activities of catalysts containing natural kieselguhrs of marine and fresh-water origin were similar.

Comparison of the catalysts containing natural kieselguhrs showed that the more active ones contained smaller amounts of soluble iron. The kieselguhrs had been heated in 8 *N* nitric acid for 2 hr to remove any impurities that would have been dissolved and reprecipitated during catalyst preparation, and the resulting solutions were analyzed for aluminum, iron, calcium, phosphate, and sulfate. Such a comparison is, of course, not valid for the calcined and flux-calcined kieselguhrs, and it is not surprising that only very small amounts of impurities were removable from Johns-Manville II and Hyflo-Super-Cel. The lower activity of catalysts containing the latter kieselguhrs could probably be attributed to their low surface areas or the orderly crystal structure of the silica, or both. Hyflo-Super-Cel produced a sharp x-ray diffraction pattern for cristobalite, and Johns-Manville II a weak cristobalite pattern; the natural kieselguhrs produced amorphous x-ray patterns. From the above results, it would appear desirable to use an acid-extracted, natural kieselguhr in the preparation of precipitated cobalt catalysts.

No correlation was observed between catalyst activity and particle size or the external or internal structure of the natural diatoms. For example, the activities of catalysts prepared from kieselguhrs with very small particle size, Snow Floss and Portuguese, were 86.6 and 166.3 cc per g per hr, respectively; this was the maximum difference observed in the tests with catalysts containing natural kieselguhrs. It is possible that the effect of differences in surface area, particle size, and structure was obscured by the influence of iron or other impurities, and by the rather wide variability in activity of different batches of catalyst prepared with the same kieselguhr.

[62] R. B. Anderson, A. Krieg, B. Seligman, and W. Tarn, *Ind. Eng. Chem.*, **40**, 2, 347–50 (1948).

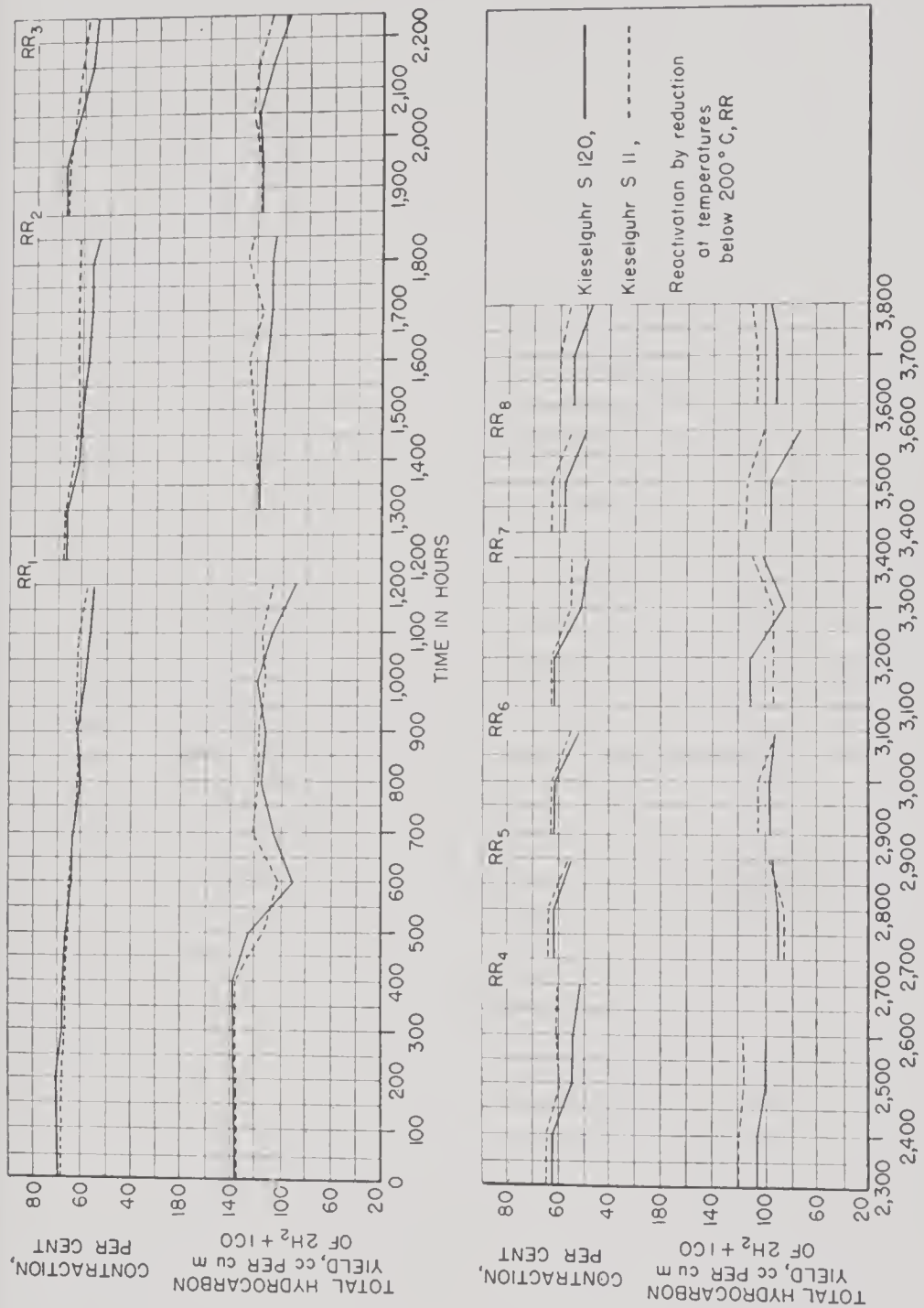


FIGURE 3–23. Effect of type of kieselguhr upon life and yields of cobalt catalysts, Ruhrchemie, 1938. ($100Co:18ThO_2:200$ kieselguhr catalyst operated at atmospheric pressure of $2H_2 + 1CO$ and 185°–195°C.)

Reproduced from reference 63.

A study made in 1938 at Ruhrchemie [29, 63] showed that the calcined kieselguhr, S.120, was a less desirable carrier than the natural kieselguhr, S.11, with respect to the life of the cobalt catalyst. The wax produced on a catalyst containing S.120 was less easily removed during reactivation of the catalyst by hydrogenation than the wax from the catalyst containing S.11. A catalyst containing S.120 retained more adsorbed hydrocarbon products and thus presented a less accessible surface for further synthesis. Figure 23 shows the course of life tests of two samples of $100Co:18ThO_2:200$ kieselguhr catalyst deposited upon kieselguhr S.120 and S.11, respectively. Synthesis was carried out at 185°–195°C with $2H_2 + 1CO$ gas at a throughput of 1 l per g of cobalt per hr, using a catalyst charge corresponding to 4 g of cobalt; the pressure was atmospheric. During the first 50 days, the contractions and yields of hydrocarbons were similar; during the remaining 105 days, the catalyst containing kieselguhr S.11 produced 15–20 per cent higher yields.

In each test, the catalyst was reactivated 8 times by passage of $75H_2:25N_2$ at a temperature 5°–7°C higher than synthesis temperature. The highest temperature was 200°C. The other conditions of reactivation—space velocity and duration—were not reported. However, on a large scale, a gas rate of 1,000 cu m per reactor per hr was used for 7–10 hr at a temperature 5°C higher than the last synthesis temperature (Ruhrchemie) or always at 200°C (Essener Steinkohle). The composition of the products obtained by this treatment depended upon the amount of hydrogen used. From the normal large-scale treatment, the product consisted of about 60 per cent of methane and 40 per cent of saturated hydrocarbons boiling below 200°C. The organic material not removed by hydrogenation was called the "Restbeladung" and consisted of residual catalyst wax. It was recovered by extraction in the laboratory with benzene and was obtained as a dark-brown solid, mp about 90°C, which had an odor of oxygenated compounds. The total amount of wax was calculated from the results of the hydrogenation and extraction treatments.

To demonstrate the effect of the nature of the kieselguhr upon the paraffin content of the two catalysts mentioned above, a sample of each catalyst was tested in the hydrocarbon synthesis under the conditions described above. At the end of 50 days, the first reactivation by hydrogen and the first extraction by benzene were carried out. On another sample of the catalyst, the procedure was repeated up to and including the hydrogen treatment. Synthesis was then started for the second period, at the end of which hydrogen revivification and benzene extraction analyses of the catalyst were performed. In this manner, the suc-

[63] Ruhrchemie, 1938, F.I.A.T. Reel K21, Frames 1,036–9.

ceeding determinations were made. The results are summarized in Table 25 and Figures 24 and 25. The paraffin contents of the catalysts containing S.11 and S.120, respectively, both before and after hydrogen reactivation, are shown in Figures 24 and 25. In the curves in Figure

TABLE 25. EFFECT OF THE TYPE OF KIESELGUHR ON THE FORMATION AND RETENTION OF WAX ON 100Co:18ThO_2:200 KIESELGUHR CATALYSTS

Synthesis Period	Reactivation Temperature, °C.	Cumulative Time, days	Catalyst Wax								
			Kieselguhr S.120					Kieselguhr S.11			
			Total Wax		Restbeladung [a]			Total Wax		Restbeladung [a]	
			g	Per Cent of Co	g	Per Cent of Total Wax	Per Cent of Co	g	Per Cent of Co	g	Per Cent of Total Wax	Per Cent of Co
1	188	50	22.1	552	12.0	54	300	21.5	538	7.8	36	195
2	190	78	21.5	538	15.0	70	375	18.6	465	10.0	54	250
3	190	96	20.4	510	16.8	82	420	16.5	413	10.8	65	270
4	192	112	21.5	538	17.0	79	425	15.7	393	10.2	65	255
5	193	121	18.4	460	15.6	85	390	12.5	313	9.6	77	240
6	194	131	18.7	468	15.8	85	395	13.4	335	11.0	82	275
7	194	144	17.6	440	15.4	87	385	13.8	345	12.0	87	300
8	200	155	19.0	475	17.0	90	425	16.0	400	13.5	84	340

[a] Organic material not removed from catalyst during reactivation by hydrogen. It was recovered by extraction with benzene and was a dark-brown solid, mp about 90°C, which had an odor of oxygenated compounds.

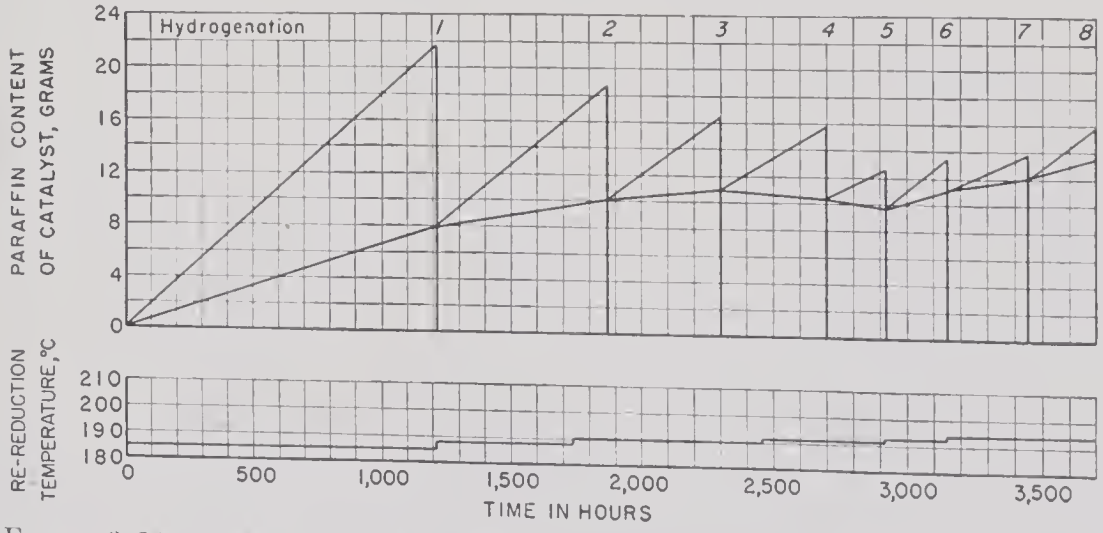


FIGURE 3-24. Paraffin content of catalyst containing kieselguhr S.11. Reproduced from reference 63.

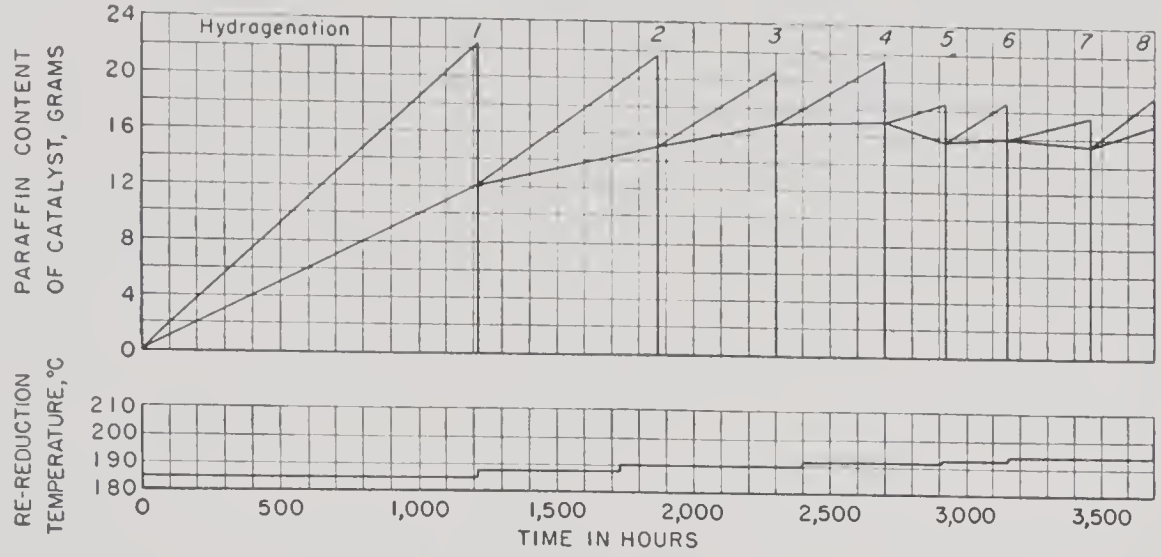


FIGURE 3–25. Paraffin content of catalyst containing kieselguhr S.120. Reproduced from reference 63.

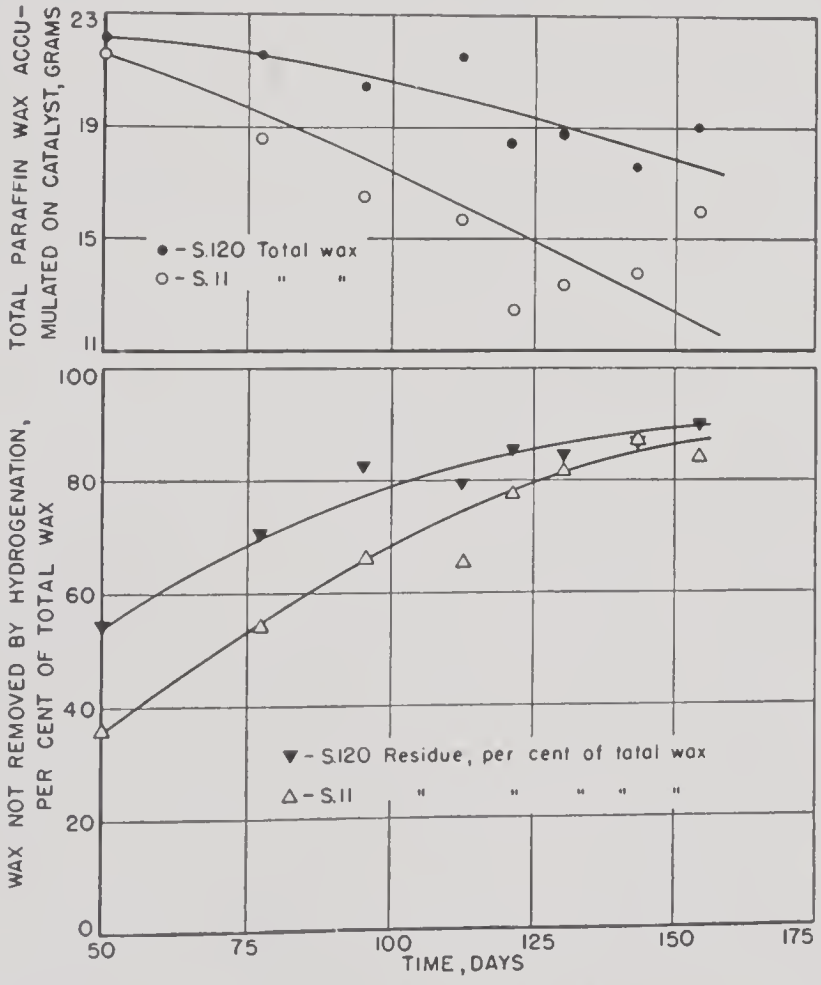

TOTAL PARAFFIN WAX ACCUMULATED ON CATALYST, GRAMS
● - S.120 Total wax
○ - S.11 " "
WAX NOT REMOVED BY HYDROGENATION, PER CENT OF TOTAL WAX
▼ - S.120 Residue, per cent of total wax
△ - S.11 " " " " "
TIME, DAYS

FIGURE 3–26. Effect of kieselguhr upon accumulation and removal of catalyst wax. Reproduced from reference 63.

26, the accumulation and retention of catalyst wax as a function of time are compared for the two kieselguhrs. The results demonstrate that the total wax accumulated on the catalyst and retained after hydrogenation was smaller in the catalyst precipitated on S.11.

The distribution of products appeared to be fairly independent of the type of kieselguhr used as a carrier, and dependent chiefly upon the density of the catalyst. However, the density of the catalyst varied directly

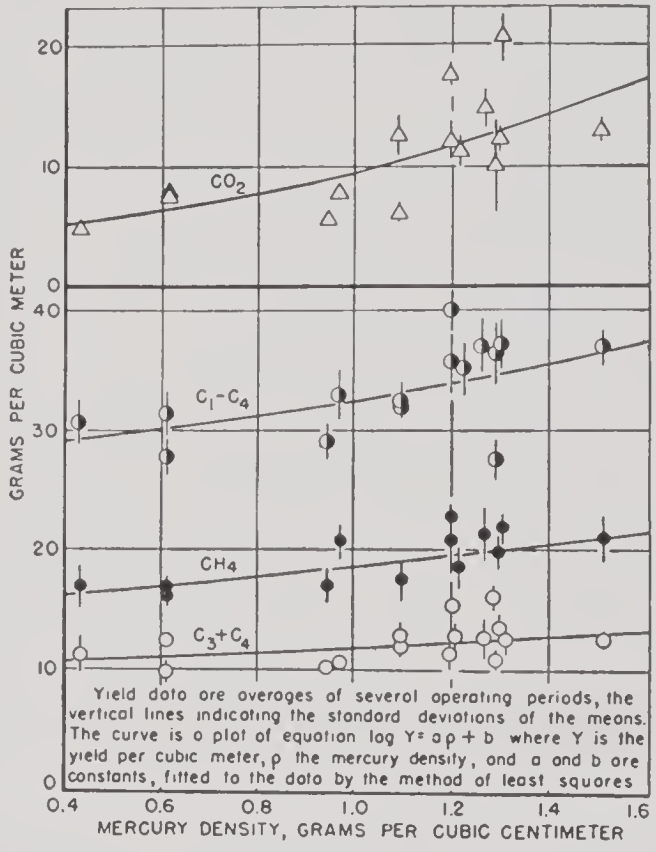

GRAMS PER CUBIC METER
MERCURY DENSITY, GRAMS PER CUBIC CENTIMETER
CO_2
C_1-C_4
CH_4
C_3+C_4
Yield data are averages of several operating periods, the vertical lines indicating the standard deviations of the means. The curve is a plot of equation log Y= aρ + b where Y is the yield per cubic meter, ρ the mercury density, and a and b are constants, fitted to the data by the method of least squares

FIGURE 3–27. Variation in product distribution with mercury density of Co-ThO_2-MgO-kieselguhr catalysts tested at atmospheric pressure, with contractions maintained at 70 per cent. Reproduced by permission from reference 62.

with that of the carrier. With granular Co-ThO_2-MgO-kieselguhr catalysts, the relationship between mercury densities (determined by the displacement of mercury at atmospheric pressure) of catalyst and kieselguhr was linear, but the density of pelleted catalysts depended upon both the density of the kieselguhr and the pelleting procedure. However, with the same setting of the pelleting machine, the density of the pellets varied directly with that of the carrier. The variation in distribution of the light hydrocarbons as a function of mercury density of the catalyst is shown in Figure 27.[62] With increasing mercury density of the catalysts, the yields of the less desirable products—CH_4, $C_3 + C_4$, C_1–C_4, and CO_2—increased at the expense of the yield of liquid products. The

points were scattered because of the many variables involved in preparing and testing catalysts, but the trends were obvious.

The function of the carrier appears to be more complex than that of a diluent or bulking agent. The U. S. Bureau of Mines studies showed that the unreduced catalyst had a higher area than the sum of the area of cobalt oxide-promoter complex plus kieselguhr; the areas of catalysts containing calcined and flux-calcined kieselguhrs were larger by about 8 per cent, and those with natural kieselguhrs, by about 20 per cent.[53, 62] There are two possible explanations: first, the fine structure of the natural kieselguhr stabilized the cobalt oxide-promoter complex at the time of precipitation; second, a fraction of the cobalt was attached to the silica skeleton of the kieselguhr by cobalt hydrosilicate bonds (see Chapter 2). The calcined kieselguhrs, being considerably less soluble, would undergo this process to a smaller extent. The role of the carrier as a bulking agent was, nevertheless, important. Kieselguhr provided a framework about which the metal oxide complex shrank when reduced to the metal.[54] Excessive decrease in the area of the metal, as a result of sintering, was inhibited during reduction and decrease in bulk volume of the catalyst was prevented. The bulk volume of kieselguhr-free preparations decreased several-fold during heating and reduction. These observations confirmed the suggestion made by Roelen [35] that kieselguhr as a carrier in cobalt and nickel catalysts produced the proper degree of dispersion of the active metal and gave the desired porosity. They were also in agreement with the report of Craxford [64] that a catalyst prepared with natural kieselguhr had a surface area and activity greater than those of a catalyst containing calcined kieselguhr.

EFFECT OF CATALYST COMPOSITION UPON ACTIVITY AND PRODUCT DISTRIBUTION

During the period 1933–1939, an enormous amount of catalyst testing occurred. Preparations of nickel, cobalt, and cobalt-nickel combined with a large number of promoters and deposited on many carriers were tested. Among the promoters were the following: MgO, CaO, SrO, BaO, BeO, Al_2O_3, La_2O_3, CeO_2, ThO_2, Cr_2O_3, UO_2, U_3O_8, SnO_2, Bi_2O_3, CdO, ZnO, Cu, Ag, Mn, and Fe. These were tested alone and in combination. Mn, UO_2, U_3O_8, ThO_2, BeO, Al_2O_3, and MgO were reported as suitable promoters. Kieselguhr, fuller's earth, asbestos, silicic acid, diatomite, silica gel, pumice, kaolin, talc, aluminum oxide, magnesium oxide, and porcelain were used as carriers. Of these, kieselguhr, kaolin, and aluminum oxide, when suitably prepared, were satisfactory. A high propor-

[64] S. R. Craxford, *Fuel*, **26**, 119–23 (1947).

tion of these catalysts was satisfactory with respect to productivity, life, or product distribution, but none surpassed the Ruhrchemie standard Co-ThO_2-kieselguhr and Co-ThO_2-MgO-kieselguhr catalysts. The summary of results that is presented below indicates the types of catalyst compositions studied and is not intended as a comprehensive survey.

Literature Review

Japanese workers reported that nickel plus 20 per cent of manganese oxide and 4–8 per cent of thoria, alumina, tungstic oxide, or uranium oxide, mixed with 1.25 times its weight of kieselguhr, yielded 100–160 cc (70–112 g) of liquid hydrocarbons per cu m of $2H_2 + 1CO$ per pass at a space velocity (volumes of gas per volume of catalyst per hour) of about 150 and at optimum temperatures in the range 185°–210°C.[65–67] Cobalt catalysts containing 5–10 per cent of copper, 4–12 per cent of manganese oxide, and 4–12 per cent of thoria, alumina, or uranium oxide mixed with 1.25 times their weight of kieselguhr yielded 120–170 cc (84–119 g) of liquid hydrocarbons per cu m of $2H_2 + 1CO$ per pass under the same conditions of space velocity and temperature as given above for nickel catalysts.[65–67] The cobalt catalysts were prepared by impregnation of kieselguhr with the metal nitrates and subsequent decomposition by roasting; their activity when thus prepared was about the same as when they were produced by precipitation from aqueous solutions.[68] The precipitation method was, however, preferable for the preparation of nickel catalysts.[69]

The I.G. Farben. laboratory at Oppau [70] reported that a cobalt catalyst containing 1 per cent of silver and precipitated upon fine-pored silica gel was as efficient as the Ruhrchemie standard Co-ThO_2-kieselguhr catalyst. In addition, it was reported to have the advantages of a saving in thorium, of reproducibility in the synthesis reactor, and of longer catalyst life.

In 1938, the I.G. Farben. laboratory at Leuna [71] reported two active cobalt catalysts, one promoted by uranium and the other by magnesium.

[65] K. Fujimura and S. Tsuneoka, *J. Soc. Chem. Ind. Japan*, **36**, Suppl. Binding, 119–21, 413–6 (1933).

[66] G. Kita, *J. Fuel Soc. Japan*, **16**, 60–2 (1937).

[67] S. Tsutsumi, *ibid.*, **16**, 55–60 (1937).

[68] S. Tsutsumi, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **35**, 481–6 (1939); **36**, 47–52 (1939).

[69] S. Tsutsumi, *ibid.*, **36**, 251–61 (1939).

[70] H. Zorn, The CO-H_2 Synthesis at I.G. Farben., PB 97,368 (1949); *F.I.A.T. Final Rept.* 1,267 (1949).

[71] T.O.M. Reel 134, Section 1a, Item 8.

Catalyst WK925, of composition 40Co:20U_3O_8:40 kieselguhr, parts by weight, and containing 0.01 per cent sodium, was prepared by a slow procedure, as follows: At room temperature, a 15 per cent solution of Na_2CO_3 was added with vigorous agitation over a period of 5 hr to a 15 per cent solution of $Co(NO_3)_2 \cdot 6H_2O$ in which the kieselguhr was suspended. A 10 per cent excess of the stoichiometric equivalent of precipitant was used. Separately, a 20 per cent ammonia solution was added to a 15 per cent uranyl nitrate solution [$UO_2(NO_3)_2 \cdot 6H_2O$] until precipitation was complete. The precipitated ammonium uranate was washed by decantation with distilled water at 20°C and then repeatedly on the filter. The precipitate of ammonium uranate was ground into the cobalt-kieselguhr slurry by mixing the two components in a porcelain ball mill for several hours. This method of adding the uranium to the catalyst produced more rigid granules than simple mixing of the cobalt-kieselguhr paste with uranyl nitrate. The catalyst paste was spread on aluminum foil and dried at 100°–120°C. The dried product had a bulk density of 0.45 g per cc when broken into 1-cm cubes.

Catalyst WK1111, of composition 46.5Co:7.0MgO:46.5 kieselguhr, parts by weight, was prepared by a rapid procedure in the following manner: A solution containing the nitrates of cobalt and magnesium was added in 2 min to a 10 per cent solution of sodium carbonate at 95°–100°C. Kieselguhr 4S was added. The suspension was filtered and washed at 90°–100°C on the filter until the filtrate no longer gave a positive test for nitrate. The catalyst cake was dried in an oven at 120°C.

These catalysts were reduced on a laboratory scale at 370°C and an hourly space velocity of hydrogen of 375 for 3–4 hr. When tested for 40–50 days in water-cooled laboratory converters of 150-cm overall length and 15-mm O.D., hydrocarbon yields of 90–100 g per cu m of $2H_2 + 1CO$ (STP) in the feed gas were produced. The average composition of the synthesis gas, in volume per cent, was $70H_2$, 28CO, $0.8CO_2$, $0.4CH_4$, and $0.8N_2$. The contraction was maintained at 55–60 per cent. Reactivation of the catalysts at the end of 30–50 days of synthesis was done by extraction with xylene at a temperature 5–10°C below its boiling point or by hydrogenation at synthesis temperature (180°–200°C). At 200°C and an hourly space velocity of hydrogen of 300, the initial activity was restored in 12 hr.

Figure 28 shows the normal composition of the product obtained from I.G. Farben., Leuna,[71] cobalt catalysts of equal activity, when tested under similar synthesis conditions. Conspicuous in the distillation curve was the absence of C_2 compounds. With the increase in operating temperature that is normally required to maintain the desired conversion a gradual shift in the direction of low-boiling products was obtained.

Distillation was carried out at atmospheric pressure up to 300°–320°C. The residue consisted of solid hydrocarbons melting at 20°–50°C; the C number was 20–22 and molecular weight 280–310. The higher-molecular-weight paraffins were removed from the catalyst by extraction with solvents. The number of carbon atoms was 26 and above, and the mp 70°–90°C. The low-boiling products were relatively less saturated than the high-boiling fractions. The total amount of unsaturates depends on the nature of the catalyst and the hydrogen content and flow velocity of the synthesis gas. Table 26 shows the olefin content obtained from an I.G. Farben., Leuna,[71] cobalt catalyst containing 22 per cent of thoria.

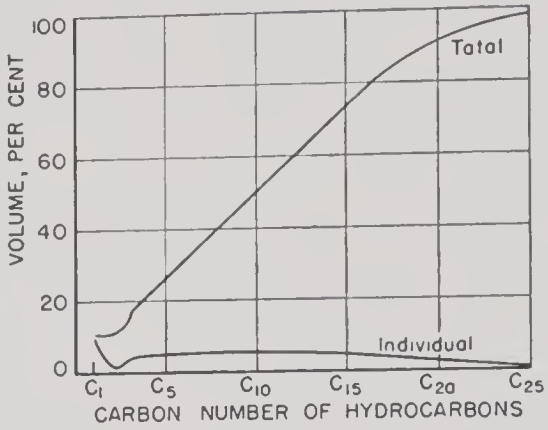


FIGURE 3–28. Distribution of hydrocarbons from cobalt catalysts. (Distillation at atmospheric pressure.) Constructed from data in reference 71.

TABLE 26. OLEFIN CONTENT OF LIQUID PRODUCT FROM Co-ThO_2 CATALYST

(I.G. Farben., Leuna, Nov. 22, 1938, converter 3.)

Boiling Range of Fraction, °C	Olefins, per cent [a]
35–100	24.0
100–125	24.3
125–150	22.5
150–175	11.8
175–200	10.2
200–225	7.3
225–250	4.6
250–275	3.8
275–305	4.0

[a] Based on Br number.

Tsuneoka and Murata [72] and Tsutsumi [73] reported that a precipitated catalyst containing equal parts of cobalt and nickel without the addition of promoters such as thoria or alumina was a poor one for the hydrocarbon synthesis. They stated that their most active catalyst was a mixture of equal parts of nickel and cobalt plus 20 per cent manganese

[72] S. Tsuneoka and Y. Murata, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **34**, 280–94 (1938); *J. Soc. Chem. Ind. Japan*, **41**, Suppl. Binding, 52–7 (1938).

[73] S. Tsutsumi, *J. Fuel Soc. Japan*, **14**, 110–6 (1935); *J. Chem. Soc. Japan*, **58**, 996–1,006 (1937); *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **35**, 435–40 (1939); *ibid.*, **36**, 335–43 (1939).

oxide, 20 per cent uranium oxide, and 125 per cent of kieselguhr (the percentages are based on the amount of nickel plus cobalt present). Katayama and his coworkers [74] reported that the activity of a cobalt-nickel(1:1)-manganese-uranium-thorium oxide catalyst was increased by approximately 10 per cent if it was oxidized at about 20°C by a slow stream (hourly space velocity of about 150) of air before its final reduction.

In 1938, Ruhrchemie [75] made tests at atmospheric pressure of $2H_2 + 1CO$ and 185°C with cobalt-nickel catalysts prepared by procedures described in Japanese publications. The results, in general, confirmed the reports of the Japanese, in that manganese, uranium oxide, thorium oxide, beryllium oxide, and aluminum oxide were good promoters for cobalt-nickel catalysts. The results summarized in Table 27 showed

TABLE 27. RUHRCHEMIE Co-Ni CATALYSTS, 1938

(Synthesis Conditions: Atmospheric Pressure of $2H_2 + 1CO$, 185°C.)

Catalyst Composition, parts by weight [a]							Av Contraction, per cent	C_5+ Product,[b] g per cu m of $2H_2 + 1CO$
Co	Ni	ThO_2	Mn	MgO	UO_2	Kg		
100	..	5	..	8	..	200	70	127
75	25	5	..	8	..	200	62	108
66	33	5	..	8	..	200	62	108
50	50	5	..	8	..	200	55	93
25	75	5	..	8	..	200	45	65
75	25	15	..	..	..	200	66	120
50	50	15	..	..	..	200	67	112
40	60	..	5	..	5	200	70	127
35	65	..	5	..	5	200	69	115
30	70	..	5	..	5	200	65	112
25	75	..	5	..	5	200	66	107
10	90	..	5	..	5	200	65	100
50	50	3	15	..	5	125	69	127

[a] Reduction temperature 250–350°C. [b] Average values for 600 hr at 185°C.

that $50Co:50Ni:3ThO_2:15Mn:5UO_2:125$ kieselguhr and $40Co:60Ni:5Mn:5UO_2:200$ kieselguhr, parts by weight of Co + Ni, were reasonably active catalysts. The catalysts containing nickel and cobalt differed

[74] I. Katayama, Y. Murata, H. Koide, and S. Tsuneoka, *ibid.*, **34**, 1,181–96 (1938); *J. Soc. Chem. Ind. Japan*, **41**, Suppl. Binding, 393–9 (1938).

[75] F.I.A.T. Reel K21, Frames 914–7.

from cobalt catalysts in the following respects: gas fraction was larger, boiling range of products was lower, saturated content of product was higher probably because of the higher hydrogenating capacity of nickel, and catalyst granules were softer. The I.G. Farben. laboratory at Oppau reported that the cobalt-nickel-manganese-uranium-kieselguhr catalyst producing the same yield as the Ruhrchemie standard cobalt-thoria-kieselguhr catalyst was noteworthy because it produced large fractions of paraffin. I.G. Farben. attributed this condensing property to the influence of the uranium.

Another method of preparing active nickel and cobalt catalysts was invented by Raney.[76] Alloys of nickel or cobalt or both with aluminum or silicon were prepared by fusion of the constituents in an induction furnace. The aluminum or silicon was subsequently dissolved by aqueous sodium hydroxide, leaving a "skeleton" of nickel or cobalt, which is a highly porous material. Fischer and Meyer [77] investigated the suitability of skeletal catalysts for the hydrocarbon synthesis. The data obtained by passing synthesis gas containing approximately 23 per cent CO and 46 per cent H_2 at atmospheric pressure over 5 g of nickel or nickel + cobalt, distributed over a layer 30 cm long, at a flow rate of 4 l per hr are summarized in Table 28. The results show that the use of silicon yielded catalysts of higher activity than those obtained from aluminum alloys, that the optimum weight ratio of nickel to cobalt was 1:1, and that the presence of kieselguhr and small amounts of potassium carbonate, copper, or manganese was undesirable. Preliminary hydrogen reduction at 350°C of nickel-cobalt catalyst prepared from nickel-cobalt-silicon alloy was not essential; reduction by hydrogen at 200°C and by hydrogen-ammonia mixture at 200°C produced a slight improvement in the activity of the catalyst. The catalyst of composition 50Ni:50Co:100Si was very dense with an apparent specific gravity of 4.5 and yielded about 20 per cent less liquid product in the hydrocarbon synthesis than was obtained by Fujimura and coworkers [78] from the same weight of nickel plus cobalt in the form of precipitated catalysts. The precipitated catalysts deteriorated more slowly than the "skeleton" alloy catalysts, which, however, were better heat conductors. Because the reaction is markedly exothermic, the improved heat conductivity would result in a lower cost of plant installation with alloy catalysts.

[76] M. Raney, U. S. Patents 1,563,587 (1925), 1,628,190 (1927), 1,915,473 (1933); *J. Am. Chem. Soc.*, **54**, 4,116–7 (1932).

[77] F. Fischer and K. Meyer, *Brennstoff-Chem.*, **15**, 84–93, 107–10 (1934).

[78] K. Fujimura and S. Tsuneoka, *J. Soc. Chem. Ind. Japan*, **36**, Suppl. Binding, 119–21, 413–6 (1933); G. Kita, *J. Fuel Soc. Japan*, **16**, 60–2 (1937); S. Tsutsumi, *ibid.*, **16**, 55–60 (1937).

TABLE 28. NICKEL, COBALT, AND NICKEL-COBALT "SKELETON" ALLOY CATALYSTS

(5 g Ni + Co, flow rate 4 l per hr of gas containing 23 per cent CO + 46 per cent H_2, atmospheric pressure.)

Composition, parts by weight	Reduction		Synthesis Conditions		Liquids, g per cu m of $2H_2 + 1CO$		
	Gas	°C	Temperature, °C	Contraction, per cent	Gasoline	Diesel Oil	Total
100Ni:100Al [a]	None		207	39	27	3	30
100Ni:100Al [a]	H_2	350	187	44	32	19	51
100Ni:100Al [b]	H_2	350	195	52	55	20	75
100Ni:200Al [b]	H_2	350	206	43	30	13	43
100Ni:400Al [b]	H_2	350	206	32	23	10	33
100Ni:46Al [b]	H_2	350	206	0	0	0	0
100Ni:100Al [c]	None		205	38	20	6	26
100Ni:100Al [c]	H_2	350	207	30	25	12	37
100Ni:100Si	None		205	37	38	16	54
100Co:100Si	None		205	40	50	18	68
50Ni:50Co:100Si [d]	None		198	55	56	40	96
50Ni:50Co:100Si [e]	None		198	51	58	32	90
50Ni:50Co:100Si [d]	H_2	350	202	47	50	28	78
50Ni:50Co:100Si [d]	None		192	54	56	30	86
50Ni:50Co:100Si	H_2	200	192	55	55	34	89
50Ni:50Co:100Si	H_2-NH_3	200	192	52	52	39	91

[a] Alloy ground in a mortar and heated on water bath in excess of sodium hydroxide for 5 hr.

[b] Pulverized alloy refluxed with sodium hydroxide for 4 hr.

[c] Contained 80 parts by weight of kieselguhr.

[d] Granules. Fused melt broken into 6-mm granules, which were refluxed for 20 hr with sodium hydroxide.

[e] Powder.

Pretreatment with hydrogen appears to be desirable for the nickel catalyst obtained from a nickel-aluminum alloy. The latter catalyst, as well as those obtained from alloys of nickel with silicon, with manganese and silicon, and with iron and aluminum, is markedly inferior to the nickel-cobalt catalyst prepared from a nickel-cobalt-silicon alloy. These results were confirmed by the investigations of Tsuneoka and his

coworkers,[79-82] who reported also that the catalyst obtained from a nickel-cobalt-magnesium alloy is a very poor one. Examination of polished and etched sections under the microscope indicates a much coarser crystal structure for it than for the nickel-cobalt-silicon alloy.[82]

Fischer and Meyer [77] reported that the best nickel catalyst was prepared by refluxing the pulverized nickel-aluminum alloy with sodium hydroxide for 4 hr. The nickel-cobalt-silicon fused melt was broken into 6-mm granules which were refluxed for 20 hr with sodium hydroxide for optimum results. The Japanese investigators [79-82] found that the optimum particle size for a space velocity of about 100 with a nickel-cobalt (1:1) catalyst prepared from the alloy nickel-cobalt-silicon (1:1:2 parts by weight) was 1–4 mm. The yield of liquid hydrocarbons was about 130 cc (93 g) per cu m of synthesis gas. The efficiency of the catalyst at constant gas input for a given amount of catalyst diminished when the free space exceeded or fell below a certain optimum value, which varied with the diameter of the reaction tube. Thus, for 10 g of nickel-cobalt (1:1) catalyst and 4 l per hr of synthesis gas, the optimum length for 13-mm tubing was about 30 cm; for 20-mm tubing it was 50 cm. If the length was shorter than the optimum, the average molecular weight of the liquid hydrocarbon product decreased and more gaseous hydrocarbons were produced. This effect was, presumably, the result of higher local temperatures when the catalyst was packed into a smaller space. If the free space exceeded the optimum value, a lower yield per pass was obtained owing to "channeling" of the gas.

At constant gas input, tube diameter, and bulk density (grams of catalyst per cubic centimeter), and with varying quantities of catalyst (*ie*, varying space velocities), a limiting value was reached that depended on other reaction conditions. A further increase in the quantity of the nickel-cobalt catalyst (decrease in space velocity) did not influence the yield of liquid hydrocarbons but increased the yield of carbon dioxide and gaseous hydrocarbons. With less than the limiting amount of catalyst (*ie*, at higher space velocities), the liquid product was of lower molecular weight and also it contained more olefins. For a tube diameter of 8 mm, a bulk density of catalyst corresponding to 10 g per

[79] S. Tsuneoka, *J. Soc. Chem. Ind. Japan*, **37**, Suppl. Binding, 738–44 (1934).

[80] S. Tsuneoka and Y. Murata, *ibid.*, **38**, Suppl. Binding, 199–212 (1935); **39**, Suppl. Binding, 267–78 (1936); **40**, Suppl. Binding, 438–49 (1937); *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **30**, 1–29 (1936); **33**, 305–12 (1937).

[81] Y. Murata, S. Tsuneoka, and S. Ishikawa, *J. Soc. Chem. Ind. Japan*, **39**, Suppl. Binding, 294–8, 325–33 (1936); *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **30**, 52–9 (1936).

[82] S. Tsuneoka and R. Kuroda, *ibid.*, **33**, 333–8, 339–46 (1937); *J. Soc. Chem. Ind. Japan*, **40**, Suppl. Binding, 449–54 (1937).

18 cm of tube length, and a gas input of 4 l per hr, the best yield obtained with 22 g of a nickel-cobalt catalyst at 180°C was 127 cc (91 g) per cu m of synthesis gas.

Product Distribution

The early German objective in studying the synthesis was to produce synthetic gasoline and motor fuel. During the ensuing years, it became apparent that these products were poorer in quality than the corresponding fractions from the hydrogenation of coal and that the higher-molecular-weight fractions were an excellent source of organic chemicals. The paraffin fraction was of considerable importance in Germany during World War II as raw material for the manufacture of synthetic detergents, soaps, and lubricants. As shown in Table 10 (p 151), paraffin wax comprised between 11 and 30 per cent by weight of the C_3+ hydrocarbon product, depending on the pressure at which the synthesis was carried out. After the conclusion of World War II, key personnel of companies operating the Fischer-Tropsch plants who were interrogated in 1945 were strongly of the opinion that under conditions of normal German peacetime economy, the process should be utilized for the production of aliphatic chemicals and special products such as waxes and high-grade lubricants, rather than fuels.[39]

It was shown in an earlier section in this chapter (p 175) that the nature of the kieselguhr influences the yields and life of the catalyst but not the distribution of products. However, the quantity of kieselguhr influences the product distribution through its effect upon the density of the catalyst. The nature of the other components in the catalyst also affects the distribution of products, as will be shown in the following pages.

In 1937–1938, Ruhrchemie [83] described the use of diluted cobalt and cobalt-nickel catalysts for increasing the low-boiling liquid fraction (boiling below 195°C). Tests made at 10 atm pressure of $2H_2 + 1CO$ and summarized in Table 29 showed that, as the cobalt content of the catalyst was decreased from 32 to 5 per cent, the temperature required to maintain the CL conversion increased from 185° to 240°C. The low-boiling oil fraction in the product increased; the Diesel oil (195°–320°C) and methane fractions remained constant; and the wax fraction decreased. In the last two experiments, in which the cobalt content was 3 and 2 per cent, respectively, the activity of the catalyst was sharply curtailed. Replacement of 25 per cent of the cobalt in catalyst 1 by nickel (experiment 8, Table 30) resulted in a product similar in distribution to that obtained in experiment 5, Table 29, in which the

[83] T.O.M. Reel 37, Bag 3,451, Item 23.

TABLE 29. RUHRCHEMIE TESTS WITH DILUTED COBALT CATALYST AT 10 ATM OF $2H_2 + 1CO$ (1937–1938)

(Reduction: 350°C, 300 l $H_2 + N_2$ per hr, $\frac{3}{4}$ hr.)

Experiment No.	1	2	3	4	5	6	7
Composition, parts by weight	100Co: 15ThO_2: 200 kieselguhr	100Co: 15ThO_2: 600 kieselguhr	100Co: 5ThO_2: 10MgO:600 kieselguhr [a]	100Co: 15ThO_2: 1,000 kieselguhr	100Co: 15ThO_2: 2,000 kieselguhr	100Co:15ThO_2: 3,000 kieselguhr	100Co:15ThO_2: 5,000 kieselguhr
Co content, per cent	32	14	14	9	5	3	2
Co density, g Co per l reduced catalyst	90	36	37	23	11	8	4.5
Temperature, °C	185	200–205	200–205	225–230	235–240	270	320
Throughput, l synthesis gas per g Co per hr [b]	1	2.4	2.4	4.2	8.4	12	21
CO converted, per cent	81	82	79	77	70	45	50
CH_4, per cent of CO converted	11	13	13	12	13	18	20 [c]
Degree of liquefaction [d]	83	82	83	82	79	Activity declined quickly. Highest yield of liquid products was 31 g per cu m $2H_2 + 1CO$.	Activity declined quickly. Amounts of liquid products insignificant.
Yields, g per cu m $2H_2 + 1CO$							
Observed	125	125	124	121	102		
Calculated [e]	147	145	149	149	138		
Distribution, weight per cent							
To 195°C (gasoline)	35	38	44	50	57		
195°–320°C (Diesel oil)	35	39	36	37	34		
Over 320°C (wax)	30	23	20	13	9		
Olefins, volume per cent							
In gasoline	19	15	19	23	23		
In Diesel oil	10	7	12	10	11		

[a] Fadenkorn.

[b] Space velocity (volume of gas per volume of catalyst per hour) was constant in all experiments.

[c] CO_2 was 14 per cent of CO converted.

[d] Defined as ratio of $C_3+:C_1+$.

[e] Calculated on the basis of 95 per cent CO conversion.

TABLE 30. RUHRCHEMIE TESTS WITH COBALT-NICKEL CATALYST AT 10 ATM OF $2H_2 + 1CO$ (1937–1938)

(Reduction: 350°C, 300 l $H_2 + N_2$ per hr, $\frac{3}{4}$ hr.)

Experiment No.	8	9	10	11	12
Composition, parts by weight	75Co:25Ni: $15ThO_2$:200 kieselguhr	75Co:25Ni: $15ThO_2$:600 kieselguhr	75Co:25Ni: $15ThO_2$:1,000 kieselguhr	50Co:50Ni: $15ThO_2$:200 kieselguhr	50Co:50Ni: $15ThO_2$:2,000 kieselguhr
Co + Ni content, per cent	32	14	9	32	11
Co + Ni density, g Co + Ni per l reduced catalyst	82	42	25	77	5
Temperature, °C	185–195	200–205	230–235	195–200	260
Throughput, l synthesis gas per g Co + Ni per hr [a]	1	2.1	3.6	1	8.4
CO converted, per cent	80	74	75	78	66
CH_4, per cent of CO converted	8	10	13	15	36
Gasol, per cent of CO converted			9	16	..
Degree of liquefaction [b]	90	86	70	60	[c]
Yields, g per cu m $2H_2+1CO$					
Observed	111	91	93	97	..
Calculated [d]	132	117	118	118	..
Distribution, weight per cent					
To 195°C (gasoline)	57	59	58	60	..
195°–320°C (Diesel oil)	33	35	40	33	..
Over 320°C (wax)	10	6	1	7	..
Olefins, volume per cent					
In gasoline	12	23	25	12	..
In Diesel oil	7	16	19	5	..

[a] Space velocity was constant in all experiments.
[b] Defined as ratio of C_3+: C_1+.
[c] Liquefaction small. At 66 per cent CO converted, the yield of liquid products was only 42 g per cu m $2H_2 + 1CO$.
[d] Calculated on the basis of 95 per cent CO conversion.

catalyst composition was 100Co:$15ThO_2$:2,000 kieselguhr. The product from the nickel-containing catalyst was more saturated. The synthesis temperature was much lower (185°–195°C) in experiment 8 than in experiment 5. Dilution of the catalyst containing 75Co:25Ni (experiments 9 and 10, Table 30) produced no further change in the −195°C fraction but did increase the Diesel oil fraction. The total yields from the nickel-containing catalysts were smaller than those from the cobalt catalysts. The product distribution from experiment 11 (50Co:50Ni) was similar to that obtained in experiment 8. Even larger low-boiling oil fractions were reported from 50Co:50Ni:$15ThO_2$:(2–5)Mn:200 kieselguhr catalysts operated at 190°–193°C (as compared with 195°–200°C in experiment 11, Table 30) and 10 atm of $2H_2 + 1CO$, as shown

Table 31. Ruhrchemie Tests with Cobalt-Nickel Catalysts at 10 atm of $2H_2 + 1CO$ (1938) at Normal Throughput [a]

Catalyst	50Co:50Ni:15ThO_2: 2Mn:200 Kieselguhr			50Co:50Ni:15ThO_2: 5Mn:200 Kieselguhr		
Temperature, °C	193			190		
Contraction, per cent	49			47		
CO conversion, per cent	64			60		
To CH_4, per cent	30			25		
H_2 conversion, per cent	69			67		
CO + H_2 conversion, per cent	66			64		
Use ratio, H_2:CO	2.16			2.18		
Yields	Gasol	C_5+	total	Gasol	C_5+	total
g per cu m feed gas	10	75	85	8	70	78
Product distribution						
Boiling range, °C	<200	200–320	>320	<200	200–320	>320
Weight per cent	72	24	4	69	27	4
Olefins, volume per cent						
Gasoline, <200°C	22			20		
Diesel oil, 200°–320°C	11			8		
Octane number, gasoline	31			..		

[a] Presumably 1 l synthesis gas per g Co + Ni per hr

in Table 31.[84] In these experiments, the methane yield was high and the total yields low.

Additional data, obtained during synthesis at 10 atm of $2H_2 + 1CO$ and temperatures of 170°–190°C at the Ruhrchemie Sterkrade laboratories and summarized in Tables 32 and 33, show the shift in distribution of the products from a predominantly low-boiling oil to a high-molecular-weight wax, with change in catalyst composition. The catalyst which produced a large wax fraction contained no nickel and less than the normal amount of kieselguhr; its composition was 100Co: 15ThO_2:140 kieselguhr.

Other tests showed that a high wax fraction could be obtained from catalysts containing very small quantities of kieselguhr. When the thoria was replaced by manganese oxide, the catalyst was operated at a significantly low temperature and produced high paraffin yields. Roelen [29,35,85] reported in 1940 that a cobalt catalyst containing manganese was active at a temperature of 165°–170°C and produced large quantities of solid paraffin. This catalyst, whose optimum composition was 100Co:15Mn:12.5 kieselguhr, was prepared as follows: A solution of cobalt and manganese nitrates containing 25 g Co and 3.75 g Mn in

[84] F.I.A.T. Reel K21, Frames 906–10, 1,119–21.

[85] F.I.A.T. Reel K21, Frames 1,093–7.

TABLE 32. EFFECT OF COMPOSITION OF Co AND Co-Ni CATALYSTS UPON DISTRIBUTION OF PRODUCTS

(Pressure synthesis using $2H_2 + 1CO$; amount of catalyst, 4–8 g of Co or Co + Ni; throughput of gas, 4–8 l per hr.)

Catalyst No.	Composition	Pressure, atm	Temperature, °C	Hours of Test	Hydrocarbon Products			
					Liquids, g [a] per cu m		Catalyst Wax [b]	
					Av	Max	Per Cent of Co	g [a] per cu m
13	100Co:15ThO_2: 140 kieselguhr	10	175–190	600	100	124	Not observed	
15	100Co:15CeO_2: 140 kieselguhr	10	170–195	180	55	63	Not observed	
17	100Co:13.5ThO_2: 225 kieselguhr [c]	10	175–185	353	65	102	640	23
20	100Co:18ThO_2: 400 kieselguhr	3	170–190	329	56	72	750	16
27	100Co:15ThO_2: 140 kieselguhr [d]	10	170–175	332	35	43	248	13
25	90Co:10Ni: 15ThO_2:200 kieselguhr	10	170–190	543	65	77	612	15
24	75Co:25Ni: 15ThO_2:200 kieselguhr	10	170–185	543	50	75	312	8
18	53Co:47Ni: 25ThO_2:160 kieselguhr	10	170–190	525	54	69	250	5

[a] Per cubic meter $2H_2 + 1CO$.
[b] Determined by extraction of catalyst with benzene.
[c] Precipitated with $(NH_4)_2CO_3$.
[d] Used $CO:H_2 = 1:2.8$.

500 cc distilled water was heated to boiling and added quickly to a stirred boiling solution containing 62 g anhydrous sodium carbonate dissolved in 750 cc distilled water. Immediately, 3.2 g kieselguhr was stirred in. The kieselguhr had previously been washed with hot nitric acid and then heated to 500°–600°C. The catalyst mixture was filtered

at once, washed with 3 l of hot distilled water, and then dried in air at 60°–75°C. It was reduced at 400°C for 1 hr with a mixture of 75 per cent hydrogen–25 per cent nitrogen passed at a space velocity of 6,000 (volumes of gas per volume of catalyst per hour). Synthesis at 10 atm of synthesis gas containing $2H_2 + 1CO$ at a space velocity of 100 and a

Table 33. Properties of Liquid Products of Co and Co-Ni Catalysts

Catalyst No.[a]	24		27	20	13
Hours of Test	1–279	279–543	332	329	600
Density at 15°C	0.747	0.726	0.735	0.751	The product had the character of "Gatsch," soft wax
Olefin, volume per cent	.....	10	4	.....	
Neutralization number	.....	.....	.....	.....	
Saponification number	.....	10.2	4.9	.....	
Cloud point, °C	− 8	−16	−10	+ 4	
Pour point, °C	−18	−22	−20	− 1	
Weight per cent					
Light oil, <200°C	63	58	58	42	24
Middle oil, 200°–320°C	31	33	36	44	25
Wax, >320°C	6	9	6	14	51 [b]

[a] See Table 32.

[b] This fraction was distributed as follows: 50 per cent, mp 47°C; 28 per cent, mp 78°C; 22 per cent, mp 101°C.

temperature that was increased from 160° to 175°C during a period of 5 months produced 120 g C_3+ hydrocarbons per cu m of feed gas. This corresponded to 75 per cent conversion of carbon monoxide. During the first 3 months the composition of the products changed, as shown in Table 34.

In 1941,[86] the Ruhrchemie reported a comparative study of the thorium- and manganese-containing wax-producing catalysts. They were precipitated and washed under normal conditions. The cobalt density of the unreduced catalyst was 150 g per l; the bulk density of the catalyst 340 g per l. It was observed, as shown in Table 35, that the

[86] F.I.A.T. Reel K21, Frames 991–3, 1,116–8.

TABLE 34. PRODUCTS OBTAINED FROM 100Co:15Mn:12.5 KIESELGUHR CATALYST

Fraction, per cent	Boiling Range, °C	Time, hr			
		1–552	552–1,099	1,099–1,720	1,720–2,240
Gasoline	<200	21.0	13.9	6.1	5.0
Diesel oil	200–320	20.5	16.0	14.7	16.7
Soft wax	320–460	25.8	22.9	23.8	21.5
Hard wax	>460	32.7	47.2	55.4	56.8
Total wax	>320	58.5	70.1	79.2	78.3

TABLE 35. RUHRCHEMIE WAX-PRODUCING CATALYSTS

(Synthesis at 10 atm of $2H_2 + 1CO$ and space velocity of 100.)

Catalyst	100Co:15ThO_2:12.5 Kieselguhr			100Co:15Mn:12.5 Kieselguhr		
Temperature, °C	175–178			165–168		
Contraction, per cent	70			60		
CO conversion, per cent	85			65		
To CO_2, per cent	0			0		
To CH_4, per cent	10			11		
Liquefaction ratio, $C_3+:C_1+$	90			89		
H_2 conversion, per cent	87			68		
CO + H_2 conversion, per cent	86			66		
Use ratio, H_2:CO	2.02			2.05		
End-gas analysis	CO_2	C_nH_m	CO	CO_2	C_nH_m	CO
Volume per cent	42.8	0.3	11.6	33.2	0.2	18.5
	H_2	CH_4	N_2	H_2	CH_4	N_2
Volume per cent	17.5	11.1	16.7	29.0	6.2	12.9
Yield	Gasol	C_5+	Total	Gasol	C_5+	Total
g per cu m feed gas	15	130	145	15	130	145
Product distribution						
Boiling range, °C	<200	200–320		<200	200–320	
Weight per cent	22	24		20	16	
Boiling range, °C	320–460	>460	Total	320–460	>460	Total
Weight per cent	21	33	54	22	42	64
Olefins	<200	200–320		<200	200–320	
Volume per cent	16	12		18	12	

manganese-containing catalyst produced better paraffin yields and operated at a significantly lower temperature. The soft paraffin fraction (320°–460°C) was fairly constant under various synthesis conditions and in the presence of various catalysts; the increased wax content was found to be in the hard paraffin (>460°C) fraction. The life of both catalysts in this investigation was 3,500–5,000 hr. The large-scale use of manganese was undesirable in cobalt catalysts for several reasons: (1) it produced too soft a catalyst; (2) it was sensitive to overheating during drying; (3) it tended to form carbon quickly; and (4) it introduced difficulties in the regeneration of the catalyst as a result of the precipitation of manganese dioxide, which clogged the filters.

The effect of variation in thoria content of cobalt catalysts upon product distribution was shown by Fischer [17] in 1932. The results of 1,600-hr tests at atmospheric pressure of $2H_2 + 1CO$ are shown in Table 36. A maximum yield of liquid hydrocarbons was produced when

Table 36. Effect of ThO_2 Content of Co-ThO_2-Kieselguhr Catalysts upon Distribution of Products

(Atmospheric pressure of $2H_2 + 1CO$, 1,600 hr, Co:kieselguhr = 100:100.)

ThO_2, per cent by weight of Co	Calculated Weight of Catalyst, g	Paraffin Extracted from Catalyst			Liquid Hydrocarbon Products, g per cu m $2H_2 + 1CO$
		Weight Per Cent of Co	Weight Per Cent of Catalyst	g	
12	8.5	255	120	10.2	91 [a]
18	8.7	290	133	11.6	..
24	9.0	380	169	15.2	17 [a]

[a] After 570 hr of synthesis.

the catalyst contained 18 per cent. At higher concentrations of thoria, the paraffin wax fraction was markedly larger and the liquid hydrocarbon fraction smaller. Accumulated paraffin, removed at the end of the test by extracting the pulverized catalyst in a Soxhlet apparatus with benzene or a fraction of synthetic gasoline for 6 or 7 hr, was equivalent to at least 250 per cent of the weight of cobalt in the catalysts. Figure 29 summarizes the results of 1,100-hr tests with varying amounts

of thoria in 100Co:200 kieselguhr S.120 catalysts, made by Ruhrchemie in 1937.[87] The contraction as an indication of catalyst activity and the paraffin contents of the catalysts, based on cobalt, are shown. Two periods of reactivation by H_2-N_2 at 500 and 900 hr are also indicated. The catalysts containing 9, 14, 18, and 24 per cent of thoria, based on cobalt, were of equal activity during the entire period; the 9 per cent

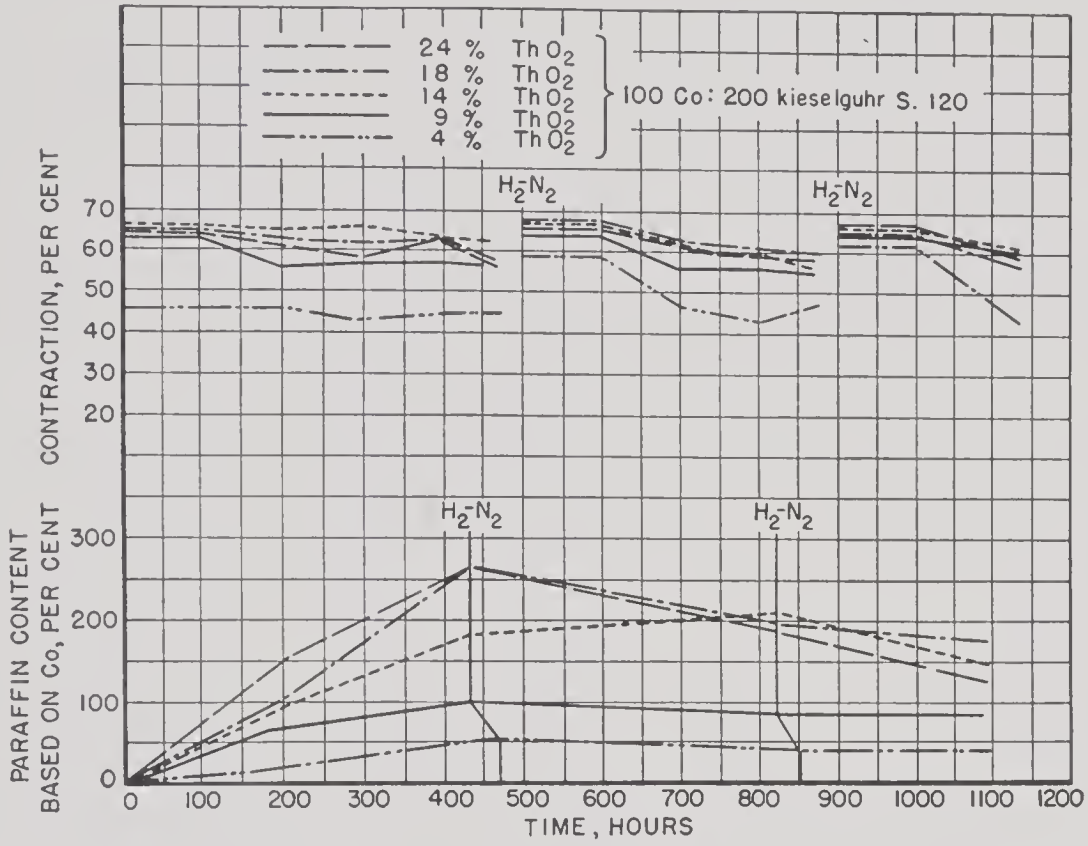


FIGURE 3–29. Effect of thoria content on cobalt catalyst activity and product distribution. Reproduced from reference 87.

ThO_2 catalyst was less active during the first 900 hr. The 18 and 24 per cent ThO_2 catalysts produced much higher catalyst wax yields (260 per cent of Co) than the others during the first 450 hr. Subsequently, these yields declined, while the catalyst wax production from the 14 per cent ThO_2 catalyst improved; at 850 hr, these three catalysts were producing about 200 per cent of catalyst wax, based on Co. The yield of catalyst wax from the 9 per cent ThO_2 catalyst did not exceed 100 per cent.

Table 37 [29] shows the relative effect of the promoters, thoria and magnesia, upon the production of catalyst wax. Three catalysts were studied at 185°C: 100Co:15ThO_2:200 kieselguhr, 100Co:5ThO_2:10MgO:200 kieselguhr, and 100Co:15MgO:200 kieselguhr. In all three catalysts, kieselguhr S.120 was the carrier. Thoria alone produced the

[87] F.I.A.T. Reel K21, Frames 976–82.

TABLE 37. EFFECT OF PROMOTERS ON CATALYST WAX

(Co:kieselguhr S.120 = 100:200, synthesis temperature = 185°C, 4 g Co.)

Synthesis Period	Cumulative Time, hr	$15ThO_2$					$5ThO_2$:10MgO					15MgO				
		Total Wax		Restbeladung [a]			Total Wax		Restbeladung [a]			Total Wax		Restbeladung [a]		
		g	Per Cent of Co	g	Per Cent of Total Wax	Per Cent of Co	g	Per Cent of Co	g	Per Cent of Total Wax	Per Cent of Co	g	Per Cent of Co	g	Per Cent of Total Wax	Per Cent of Co
1	1,550	26.0	650	22.0	85	550	19.8	495	8.4	42	210	9.0	225	0.4	4	10
2	1,850	26.6	665	20.6	77	515	12.6	315	5.6	44	140	2.4	60	0.4	17	10
3	2,250	25.2	630	21.6	86	540	11.6	290	6.0	52	150	2.6	65	0.8	31	20

[a] Organic material not removed from catalyst during reactivation by hydrogen.

largest amount of catalyst wax and magnesia the least; thoria-magnesia was intermediate.

The Ruhrchemie reported that the paraffin fraction from the conventional Fischer-Tropsch synthesis, constituting 11–30 per cent by weight of the C_3+ hydrocarbon product, comprised waxes whose melting points ranged from 40° to 110°C and whose molecular weights ranged up to 2,000. At the Ruhrchemie works at Sterkrade-Holten,[38,39] the residue boiling above 320°C from the distillation of the primary product of the medium-pressure synthesis was separated by vacuum fractionation into two distillates and a residue distilling above 460°C (at 760 mm Hg). The first fraction was "sweated" to give "soft wax" (mp 40°C); the second fraction was sweated to yield "slab wax" (mp 50°–52°C). The residue, crude "hard wax," mp 90°C, was refined with bleaching earth and sold as "refined wax." By blending 30 parts of this wax with 70 parts of soft wax, a product sold as "refined plastic wax" was obtained. By similar treatment of the residue boiling above 320°C obtained from distillation of products from the normal-pressure process and the wax extracted from the catalyst by solvent, further quantities of soft wax and a moderately hard wax sold as "catalyst wax," mp 87°–91°C, were obtained. Table 38 [38] shows the properties of the Ruhrchemie Fischer-Tropsch waxes.

The bulk of the soft wax, or "Gatsch," was oxidized to fatty acids at the Deutsche Fettsauere Werke, Witten, for use in the production of soap and edible fats. A part of these waxes was also used in the manu-

TABLE 38. PROPERTIES OF RUHRCHEMIE FISCHER-TROPSCH WAXES

Properties	Soft Wax	Slab Wax	Catalyst Wax	Refined Plastic Wax	Refined Hard Wax
Setting point, °C (rotating thermometer)	42.5	50–52	87–91	75	90
Melting point, °C	44.0	53	...	About 85	110
Flow point, °C	40.2	48–49	...	77	98
Drop point, °C	41.8	49–50	...	79	99
Iodine number	.....	2.5	3.5	2.0	2.0
Acid number	0.14	0.03	...	0.05	0.1
Saponification number	0.35	0.6	1.0	0.9	0.8
Penetrometer number	.....	35.0	About 30	17.0	4.0
Mean molecular weight	.....	380	...	500	600
Mean carbon number	.....	27	...	36	43

facture of lubricating oils. The hard and slab waxes were used in the manufacture of polishes, candles, and explosives. The plastic wax was used for impregnation of paper and cardboard.

CATALYST PRETREATMENT

Reduction

Roelen [35] believed that the success of the catalyst depended upon correct reduction. The general principle was that sintering of the catalyst must be avoided during reduction, and that this could be accomplished by conducting the reduction as quickly as possible. Hence, reduction was done (1) with the catalyst arranged in a short bed, (2) using a high rate of pure hydrogen, (3) at the lowest temperature, and (4) in the shortest time compatible with sufficient reduction. Conditions 3 and 4 being interrelated, moderate values of both factors were found to give better results than extremes of either. It was found that the most active catalysts were obtained by stopping the reduction before all the cobalt was reduced to metal. The quantity of cobalt reduced, expressed in per cent, was called the "reduction value." Most active catalysts had reduction values of 65–70; the usual technical-scale catalysts, 55–65. It was believed at the Ruhrchemie [29] that "oxidation-reduction equilibrium" was reached in the catalyst during synthesis. During the first 2 weeks in the full-scale reactors, hydrocarbon yields increased to a max-

imum because of an increase in reduction value. After that, the yields slowly decreased, as did the reduction value, the latter from 55 to 35–40. Hence, reduction value was not considered important as an indication of the activity to be expected of a catalyst, but merely as showing whether reduction had been carried too far. If the reduction value was very high, the catalyst was active for only a short period. Roelen considered that the residual unreduced cobalt oxide in the catalyst was important in preventing sintering of the cobalt.

The ease of reduction of a catalyst, or its reducibility, as defined by the temperature and time required to reach a given reduction value, varied with the composition and method of preparation. Table 39 [29, 88] shows the results of a Ruhrchemie study of the effect of composition on

Table 39. Reducibility of Cobalt Catalysts

Composition, parts by weight				Time of Reduction, min	Reduction Value
Co	ThO_2	MgO	Kieselguhr		
100	15	..	100	5	79
			200		73
			600		47
			1,000		28
			2,000		36
100	5	10	200	15	78
			600		70
			1,000		25
			2,000		33
100	..	15	100	15	64
			200		64
			600		63
			1,000		62
			2,000		53

reducibility. Samples were reduced 5 and 15 min at 400°C with 300 l per hr of $75H_2$-$25N_2$ passing over a 10-cm layer of catalyst contained in a tube 21 mm in diameter, and the fraction of cobalt reduced to metal was measured. For Co-ThO_2-kieselguhr and Co-ThO_2-MgO-kieselguhr catalysts, the reducibility decreased as the kieselguhr content was increased from 100 to 1,000 parts per 100 parts of cobalt. For cobalt-magnesia-kieselguhr catalyst, however, the reducibility was unchanged over this range of kieselguhr contents. Comparison of catalysts containing 100Co:100 kieselguhr and reduced at the same temperature

[88] F.I.A.T. Reel K21, Frames 699–700.

showed that the reducibility varied with the promoter, decreasing in the order ThO_2, ThO_2-MgO, MgO. In general, reducibility was sensitive to the presence of impurities, particularly nickel and copper, which facilitate reduction. For this reason, pure kieselguhrs and pure cobalt were desirable in the manufacture of the catalyst.

Reducibility was also investigated by reducing the catalyst for a fixed period of about an hour at a series of different temperatures and measuring the fraction of cobalt reduced. Thus, for 100Co:5ThO_2:10MgO:200 kieselguhr, 15 per cent was reduced at 300°C, 45 per cent at 325°C,

TABLE 40. REDUCTION OF COBALT CATALYST WITH H_2-N_2 IN PRESENCE OF CO_2 AND H_2O VAPOR (RUHRCHEMIE)

(2–3-mm catalyst granules, catalyst layer 20 cm long and 21 mm deep, throughput 150 l H_2-N_2 per hr, 350°C.)

Time, min	Co Metal, per cent	Off-Gas Analyses, volume per cent						
		CO_2	C_nH_m	O_2	CO	H_2	CH_4	N_2
a. H_2-N_2 + 1 per cent H_2O [a]								
25	33	1.6	0	0	0	72.4	2.1	24.9
50	50	...	..	...	...	....	...	....
100	61.5	2.0	0	0.2	0	71.3	1.1	25.4
180	66.0	...	..	...	...	....	...	....
b. H_2-N_2 + 3 per cent CO_2								
0	....	2.9	0	0	0.2	72.2	0.7	24.0
50	8.0	1.0	0	0.1	0	67.2	3.6	29.2
100	11.5	0.4	0	0.1	0	68.1	4.6	26.8
180	11.5	0	0	0	0.2	69.5	2.8	27.7
c. H_2-N_2								
35	62	...	..	...	...	....	...	....
50	81	...	..	...	...	....	...	....
65	85	...	..	...	...	....	...	....

[a] H_2 saturated at 3°C with 8 g H_2O per cu m H_2-N_2, corresponding to about 1 per cent H_2O.

and 75 per cent at 350°C. 100Co:15MgO:75MgO (magnesia as promoter precipitated on magnesia as a carrier) was very difficult to reduce: 24 per cent at 450°C. Roelen [35] suggested the following explanation for the lower reducibility of magnesia-containing catalysts. He believed that the unreduced catalyst consisted of mixed crystals of magnesium and cobalt oxides. These should be difficult to reduce on account of the insulating action of the magnesia in preventing the conduction of heat of reduction from one cobalt atom to the next. These mixed crystals should also give active catalysts because the dispersal of the cobalt throughout the mass of magnesia produced a fine subdivision of cobalt.

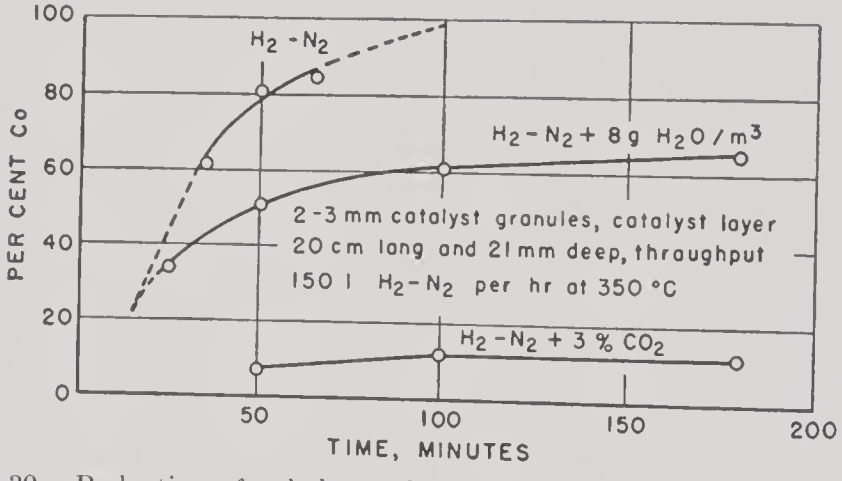


FIGURE 3–30. Reduction of cobalt catalysts in presence of CO_2 and H_2O vapor. Reproduced from reference 89.

Catalysts difficult to reduce were found in Ruhrchemie tests to be the most active and long-lived. Catalysts with very low reducibility and low reduction value attained high productivity during synthesis slowly, and sometimes required a week or 10 days to reach the "oxidation-reduction" equilibrium.

Ruhrchemie laboratory tests [89] showed that carbon dioxide and water hindered the reduction of cobalt catalysts. The data are summarized in Table 40 and Figure 30. In the presence of about 1 per cent water vapor, reduction of cobalt catalysts did not produce more than 60–65 per cent free cobalt, as compared with 85 per cent free cobalt obtained when dry H_2-N_2 was used. Increasing the quantity of water vapor further reduced the effectiveness of reduction at 350°C with 300 l H_2-N_2 per hr for $\frac{3}{4}$ hr. The off-gas analyses indicated that carbon dioxide was released from the catalyst and that methane was produced. In the presence of 3 per cent of carbon dioxide, only 11.5 per cent of free cobalt metal was produced, even after 3 hr of reduction. Analysis showed that

[89] F.I.A.T. Reel K21, Frames 792–805, April 1937.

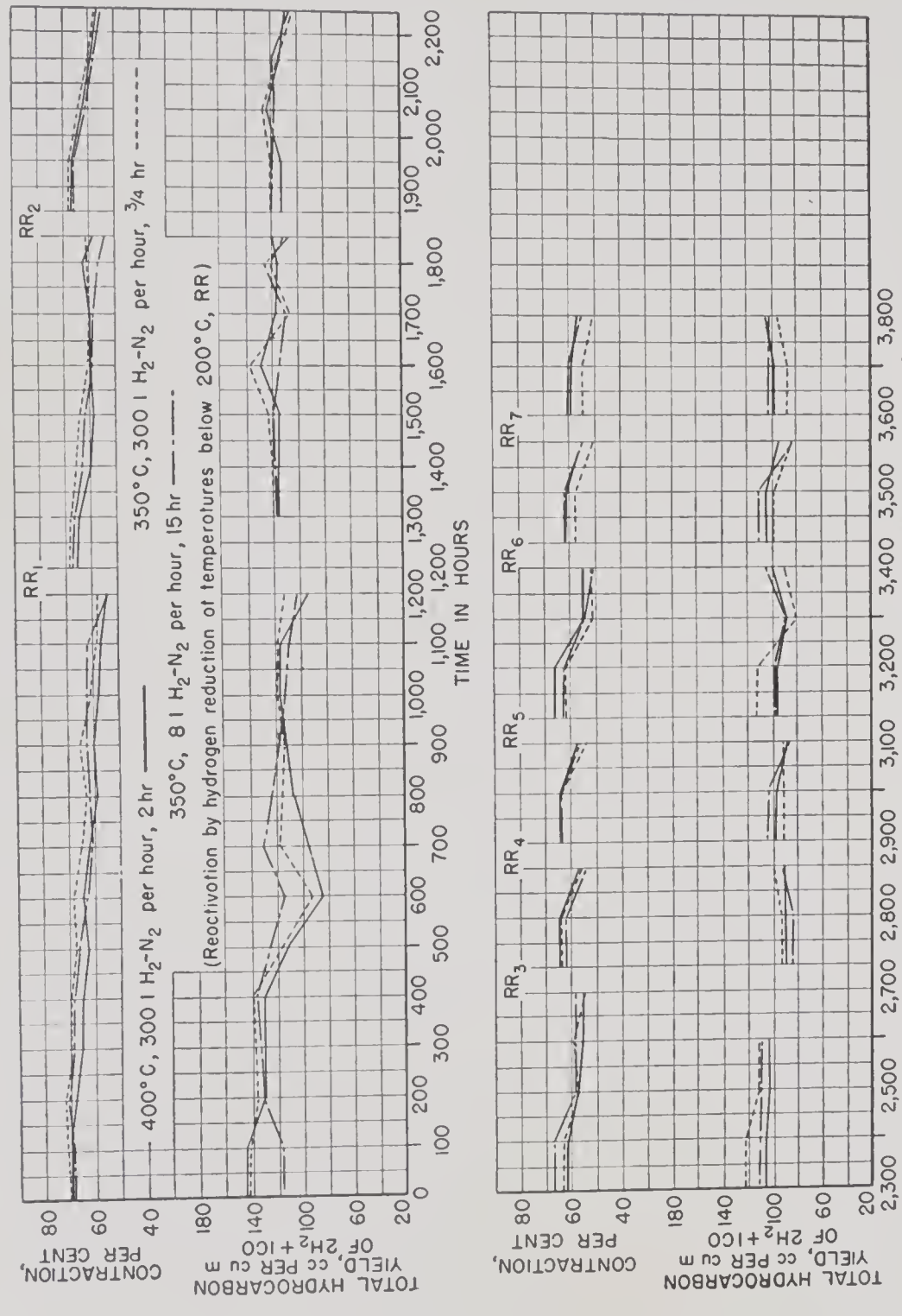


FIGURE 3-31. Effect of reduction conditions upon life and yields of cobalt catalysts, Ruhrchemie, 1938. ($100Co:18ThO_2:200$ kieselguhr catalyst operated at atmospheric pressure of $2H_2 + 1CO$ and 185°–195°C.)
Reproduced from reference 90.

the CO_2 concentration in the off gas decreased, whereas the methane increased. The CO_2 was probably hydrogenated to methane according to the reaction, $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$.

Ruhrchemie [90] conducted tests in 1938 to determine the effect of the conditions of reduction upon the life and yields of Co-ThO_2-kieselguhr (100:18:200) catalysts. The catalysts were reduced under the following conditions: 350°C, 300 l H_2-N_2 per hr, $\frac{3}{4}$ hr; 400°C, 300 l H_2-N_2 per hr, 2 hr; 350°C, 8 l H_2-N_2 per hr, 15 hr. Then each catalyst was tested in the atmospheric-pressure synthesis at 185°–195°C. Figure 31 shows the results of 3,800-hr experiments with three catalysts of equal reduction value. It is apparent that all three catalysts were similar in activity and that the effect of reduction was insignificant under these conditions.

U. S. Bureau of Mines [91] results were in agreement with those of the Ruhrchemie. The data summarized in Table 41 indicate the effect of using varying procedures for reducing and subsequently inducting (or conditioning) Co-ThO_2-kieselguhr and Co-ThO_2-MgO-kieselguhr catalysts. The following procedures were used:

Reduction procedure

A. Temperature raised from 250°C to 360°C in about 8 hr and maintained for 2 hr at 360°C; hydrogen space velocity of about 250 (volumes of gas per bulk volume of catalyst per hour).

B. Four hours at 360°C at a space velocity of 500.

C. Four hours at 360°C at a space velocity of hydrogen of 1,000.

D. Two hours at 360°C at a space velocity of hydrogen of 3,000.

E. Two hours at 400°C at a space velocity of 3,000.

Induction procedure

1. Contraction schedule—within 30 min after synthesis gas was introduced at 150°C, the temperature was increased until a contraction of 45–50 per cent was produced, 175°C being the upper limit. After 48 hr, the temperature was further increased to maintain the same contraction, 180°C being the upper limit. After 24 additional hr, the temperature was increased to produce a contraction of 70–75 per cent.

2. Temperature schedule—synthesis gas was introduced at 150°C and the temperature was increased to 175°C within an hour. After 48 hr, the temperature was increased to 180°C, and after 24 additional hr, to the temperature necessary to maintain 70–75 per cent contraction.

Induction pressure

a. Atmospheric.

b. Seven atmospheres.

[90] F.I.A.T. Reel K21, Frames 1,032–35.

[91] U. S. Bureau of Mines unpublished work.

TABLE 41. EFFECT OF REDUCTION AND INDUCTION PROCEDURE ON ACTIVITY OF COBALT CATALYSTS (U. S. BUREAU OF MINES)

Duration of Test, hr	Reduction and Induction Procedure [a]			Weight of Catalyst, g	Synthesis Conditions			Hydrocarbon Products			
					Pressure, atm	SVH [b]	Temperature, °C	g per cu m [c]			Weight Per Cent of Whole, C_5+
								CH_4	C_1–C_4	C_5+	
100Co:18ThO_2:100 kieselguhr catalyst 108B, pellets 3.2-mm diameter × 3.2-mm length											
658	*A*	2	*a*	38.8	0 [d]	100	185	13.5	27.4	84.5	75.4
891	*A*	2	*a*	38.8	7	100	189	24.4	43.1	85.5	66.5
1,000	*A*	1	*b*	36.0	7	100	187	23.7	40.7	86.3	68.0
571	*B*	2	*a*	38.0	0	100	187	17.2	37.3	86.2	69.8
1,127	*D*	1	*b*	36.5	7	100	187	29.5	49.7	82.9	62.6
801	*D*	2	*b*	36.5	7	120	191 [e]	33.1	54.1	79.0	59.4
1,094	*D*	2	*b*	37.5	7	100	186	28.5	51.0	89.5	63.8
1,143	*C*	2	*b*	36.8	7	100	187	27.2	47.1	82.7	63.8
1,141	*D*	2	*a*	37.6	0	100	181	14.7	29.2	83.8	74.2
100Co:6ThO_2:12MgO:200 kieselguhr catalyst 89K, granules 6–10 mesh											
1,045	*E*	2	*a*	16.9	1	100	186	17.1	33.4	97.0	73.9
1,040	*E*	1	*a*	16.0	1	100	188	17.6	30.2	89.5	74.8

[a] See explanatory paragraphs in text.
[b] Space velocity per hour.
[c] Per cubic meter of synthesis gas.
[d] Gauge reading.
[e] Temperature high because of higher space velocity.

Reduction of the Co-ThO_2-MgO-kieselguhr catalyst required a temperature of 400°C, as compared with 360°C used for Co-ThO_2-kieselguhr preparations. Otherwise, the conditions of reduction and induction had no significant effect upon the catalyst activity.

CARBURIZATION

When a cobalt catalyst was reduced with hydrogen and then carburized with carbon monoxide, its subsequent activity in the hydrocarbon synthesis was severely inhibited.[92] In one U. S. Bureau of Mines experiment, Co-ThO_2-MgO-kieselguhr (100:6:12:200) catalyst 89J was

[92] S. Weller, L. J. E. Hofer, and R. B. Anderson, *J. Am. Chem. Soc.*, **70**, 799–801 (1948).

reduced with hydrogen at 400°C and subsequently carbided with carbon monoxide for 20 hr at 200°C; the volume of carbon monoxide reacted was equivalent to 70 per cent conversion of the cobalt to Co_2C. Exposure of this carbided sample to circulating synthesis gas ($2H_2 + 1CO$) resulted in an overall synthesis rate at 150°C of 60–70 $\times 10^{-4}$ g C per g Co per hr. After removal of the carbide by hydrogenation at 150°–194°C and re-exposure of the sample to synthesis gas, a synthesis rate of 250–300 $\times 10^{-4}$ g C per g Co per hr was observed, an increase of 400 per cent. The distribution of the synthesis products was about the same in both cases. Treatment with hydrogen, carbon monoxide, and synthesis gas was carried out at atmospheric pressure.

In another experiment,[92] Co-ThO_2-kieselguhr (100:18:100) catalyst 108B was carbided in carbon monoxide at 210°C to an extent equivalent to 110 per cent Co_2C. The excess carbon could be accounted for as a monolayer of chemisorbed carbon monoxide. This sample was observed to have no appreciable activity in flowing synthesis gas, while a control sample, similarly reduced initially but not carbided, gave copious yields of oil and water. Partial hydrogenation of the carbided sample at 190°C, with removal of 72 per cent of the carbon which had been introduced, restored the activity to about one-half the normal value.

The loss of synthesis activity on carbiding persisted even when synthesis was continued for several days. This behavior is illustrated in Figure 32. A sample of Co-ThO_2-kieselguhr catalyst 108B was carbided with carbon monoxide for 24 hr at 200°C after initial reduction in hydrogen at 360°C. On exposure to flowing synthesis gas at 182°C, the carbided sample originally showed no catalytic activity, as measured by the fractional decrease in gas volume (contraction) as the gas passed through the converter (Figure 32*a*). During operation for 1 day at 182°C, the contraction rose to 20 per cent but did not increase further during another 18 hr of synthesis. Increasing the temperature to 190°C increased the contraction only to 33 per cent, even after a day. Subsequent hydrogenation of this sample at 210°C and re-exposure to synthesis gas resulted in a normal contraction of more than 70 per cent at 189°C (Figure 32*b*). Recarbiding the active catalyst for 24 hr at 200°C again reduced the activity to the low value observed after the first carbiding (Figure 32*c*), and rehydrogenation of the carbided sample restored the activity almost to normal (Figure 32*d*). These experiments showed clearly that carburization of reduced cobalt catalysts was undesirable. This information is important in consideration of the mechanism of the Fischer-Tropsch reaction over cobalt catalysts (see Chapter 6).

Repeated cycles of carburization and hydrogenation of carburized catalyst gradually poisoned the catalyst.[52] The surface area of freshly

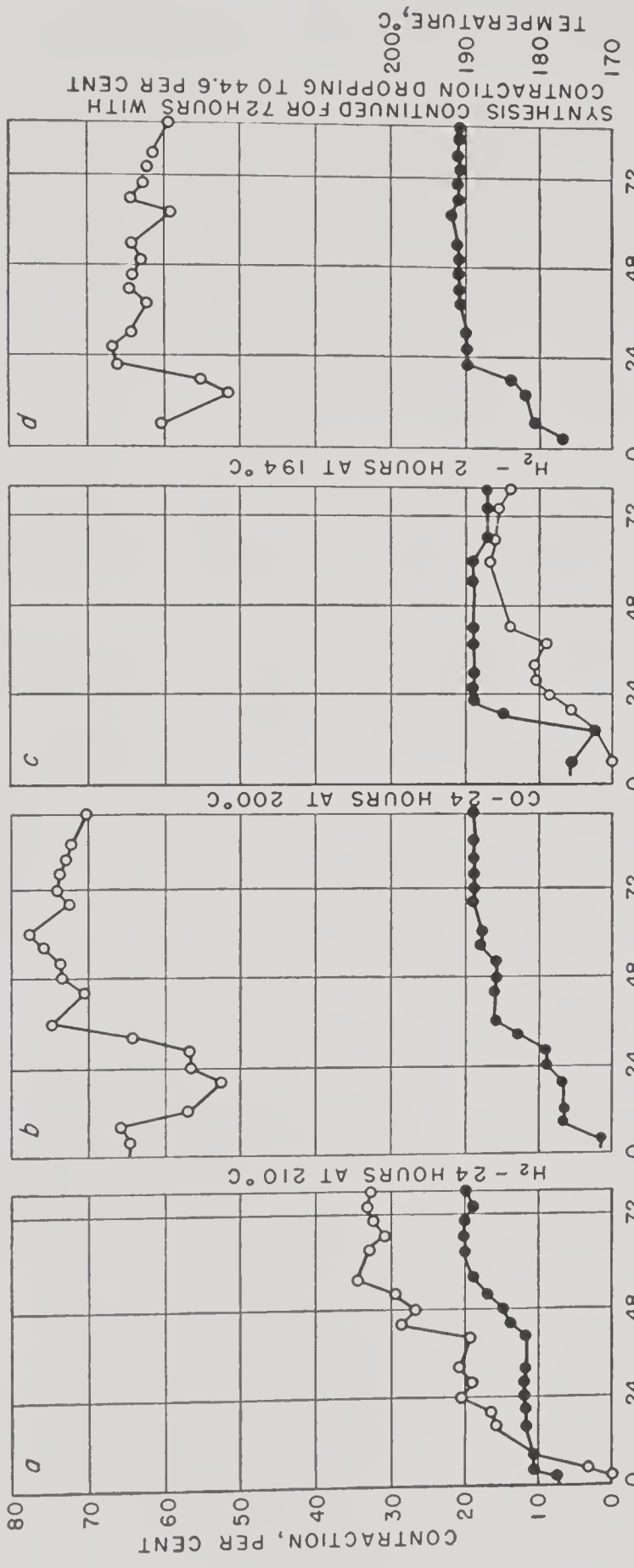


FIGURE 3–32. Apparent contraction (○) and temperature of operation (●) versus time for cobalt catalyst 108B, tested at atmospheric pressure. Reproduced by permission from reference 92.

reduced cobalt catalyst 108B, carburized and reduced at 208°C, and then carburized again at 235°C and reduced again at 208°C, was not changed. However, the volume of carbon monoxide that could be chemisorbed was sharply decreased during carburization and only partially restored during subsequent hydrogenation. Some free carbon remained on the catalyst after the last reduction. Carburization at 275°C produced chiefly free carbon, which was slowly removed by prolonged reduction at 360°C. The surface area and adsorption properties of the freshly reduced catalyst were restored, but the catalyst was still poisoned with respect to the formation of carbide at 208°C. These results showed that a change occurred in the structure of the catalyst during carburization, which affected its activity for the hydrocarbon synthesis. The magnitude of this effect was shown by the results obtained during synthesis on catalyst 108B when tested at atmospheric pressure and constant temperature and flow of synthesis ($2H_2 + 1CO$) gas. Before each carburization step, the catalyst was stripped of adsorbed hydrocarbons by hydrogenation for 2 hr at 208°C so that the surface would be accessible during carburization. After carburization at 208°C, the activity decreased and the yields of light hydrocarbons increased. Hydrogenation at 208°C partially restored the activity and increased the percentage of higher-molecular-weight products. In the succeeding carburization and reduction cycles, the activity of the catalyst declined steadily and the fractions of methane and other light hydrocarbons steadily increased. Thus, repeated cycles of carburization and reduction at 208°C caused a poisoning of the catalyst that was superimposed on the harmful effect of the presence of carbide. Subsequent hydrogenation of the catalyst at 400°C restored its activity almost to normal but did not improve the product distribution. Thus, free carbon does not appreciably affect the activity but has a marked effect upon the product distribution. Similar results were observed with the Co-ThO_2-MgO kieselguhr catalysts.

The data discussed above are presented in Chapter 6, Table 4, p 476.

REACTIVATION

The course of life tests of two Ruhrchemie samples of $100Co:18ThO_2:200$ kieselguhr catalyst deposited upon kieselguhr S.120 and S.11, respectively, was described on p 180 of this chapter. During a period of 155 days, each catalyst was reactivated eight times by passage of $75H_2$-$25N_2$ at a temperature 5°–7°C higher than synthesis temperature but not exceeding 200°C. The other conditions of reactivation—space velocity and time—were not reported. Each reactivation period occurred when the gas contraction fell below 55 per cent (Figure 23), and four times the

activity, as measured by gas contraction, was restored almost to its initial value. The last four reactivation periods (after 121 days) were less and less effective.

The reactivation procedure in the U. S. Bureau of Mines catalyst-testing laboratory was to pass hydrogen over the catalyst at a space velocity of about 100 for 2 hr at a temperature 10°C higher than the preceding synthesis temperature and then very slowly for 44 hr at 150°C. This was done at 115-hr intervals during a synthesis test. Table 42 shows the yields obtained during a test of 48 days at an average temperature of 183°C and atmospheric pressure, with cobalt-thoria-magnesia-kieselguhr catalyst 89FF.[52, 91] Although the activity decreased

TABLE 42. TEST OF PELLETED COBALT-THORIA-MAGNESIA-KIESELGUHR CATALYST 89FF AT ATMOSPHERIC PRESSURE WITH $2H_2 + 1CO$ GAS [a, b] (U. S. BUREAU OF MINES)

Time, hr	Temperature, °C	Contraction, per cent	SVH	Hydrocarbon Products, g per cu m [c]			H_2O, g per cu m [c]
				CH_4	C_1–C_4	C_5+	
114	180	57.5	109	17.3	....	58.5	140.5
115	185	69.8	110	21.7	....	82.5	171.3
114	185	71.4	117	....	....	89.0	165.8
114	182	69.1	113	....	....	81.4	174.6
114	181	69.8	113	22.7	39.7	76.2	171.2
114	183	70.4	105	22.3	48.2	137.7	176.3
115	184	72.3	113	15.0	31.8	94.4	182.0
115	184	65.5	118	23.1	36.9	90.2	174.7
115	181	64.6	123	13.2	24.9	76.3	158.6
114	183	69.0	117	13.9	18.6	70.2	175.1
115	182	66.0	119	27.8	46.8	72.7	158.0

[a] Catalyst was reduced by hydrogen for 2 hr at 400°C and an hourly space velocity of 3,000 and inducted by the temperature schedule at atmospheric pressure.

[b] Catalyst contained acid-extracted Filter-Cel kieselguhr.

[c] Per cubic meter of feed gas.

somewhat during each period, neither the average activity nor the product distribution varied significantly for the entire test. When the catalyst was removed from the reactor at the conclusion of the test, sorption and density measurements showed that hydrocarbons adsorbed on the catalyst had reduced its surface area to 5 per cent of that of the freshly

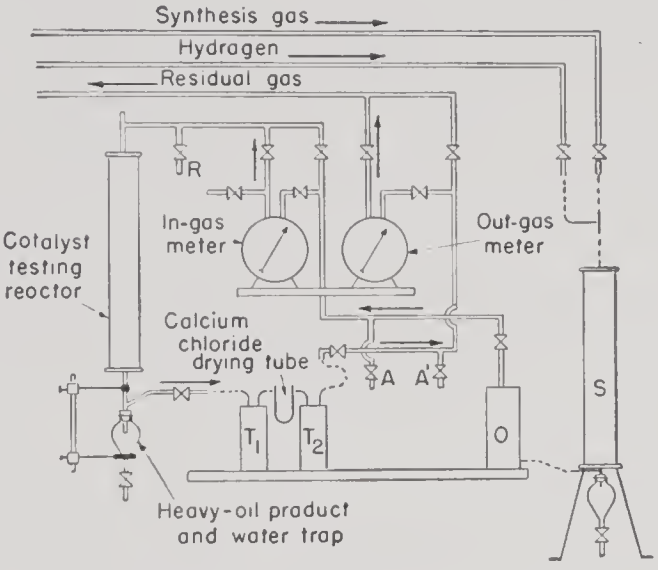
reduced catalyst (from 80.8 to 4.4 sq m per g of unreduced catalyst) and that these adsorbed hydrocarbons were located within the pellet in the pore volume (volume of pores smaller than 5 microns in diameter) and not on the external surface of the catalyst.[52] It was estimated that 80 per cent of the pore volume was filled with paraffin wax at the temperature of the synthesis, 183°C. Hydrogenation of the used catalyst under the conditions employed to reactivate the catalyst during synthesis removed about 90 per cent of the adsorbed hydrocarbons. This result indicated that most of the hydrocarbon product deposited on the catalyst during any synthesis period was removed in the succeeding reactivation period and, therefore, that the catalyst in its normal condition of operation at atmospheric pressure was heavily covered with hydrocarbons. Final reduction of the used catalyst at 400°C almost completely restored the surface to its condition when freshly reduced. The significance of these results is that the cobalt in this used catalyst was apparently not sintered; otherwise the restoration of the surface would not have been possible.

Hall and Smith [93] observed that a cobalt catalyst maintained a high state of activity for 14 months when it was tested at atmospheric pressure, with intermittent reactivation by hydrogen. The catalyst of composition $100Co:6ThO_2:3MgO:200$ kieselguhr was prepared by the rapid simultaneous mixing of boiling solutions of cobalt and thorium nitrates (40 g Co and 2.4 g ThO_2 per l), sodium carbonate (88 g Na_2CO_3 per l), and a warm, aqueous suspension of magnesia and kieselguhr (both screened through 72-mesh BSS). The quantities used were in the weight proportions: $100Co:6ThO_2:12MgO:200$ kieselguhr. The excess MgO was removed during washing of the precipitate. The mixture was boiled for 2 min with vigorous stirring, filtered rapidly, and the precipitate washed free from occluded salts with boiling distilled water. Subsequently, the filter cake was dried in air at 110°C and graded into 7–14 mesh BSS granules. The kieselguhr was a natural material of Portuguese origin, consisting mainly of small, "spindle-like" diatoms; it was washed with a cold mixture of equal parts of 50 per cent HNO_3 and 50 per cent HCl before use.

The synthesis reactor consisted of a mild steel tube 110 cm in length and 15 mm I.D. welded into a mild steel "jacket" 6.3 cm I.D., on the outer surface of which was electric heating wiring. The annular space between the outer surface of the reactor and the inner surface of the jacket was filled with aluminum alloy, which comprised the heat-dissipating and temperature-equalizing means. Two steel tubes of 6-mm I.D. were embedded in the alloy, one to act as a thermocouple pocket

[93] C. C. Hall and S. L. Smith, *J. Soc. Chem. Ind. (London)*, **65**, 128–36 (1946).

and the other to accommodate a thermoregulator. As a result of preliminary comparative tests with an additional thermocouple in the center of the reactor tube, the temperature in the aluminum jacket could be controlled to a value 1°–2°C below that required in the reactor. The catalyst was supported on a perforated sheet located 23 cm above the lower end of the aluminum jacket. A normal charge of catalyst (100



S - Organic sulfur removal from synthesis gas
O - Fe_2O_3 for H_2S removal from synthesis gas
T_1 - Ice-cooled trap for collecting remainder of water and part of light-oil product
T_2 - Dry-ice trap for collecting remainder of light oil
A, A' - Tees for sampling synthesis and residual gases, respectively
R - Hydrogen inlet for reduction of catalyst

FIGURE 3–33. Flow diagram of laboratory-scale catalyst-testing apparatus at British Fuel Research Station, 1941. Reproduced by permission from reference 93.

cc) occupied 58 cm of the reactor when the central thermocouple pocket was absent. The arrangement of the apparatus is shown diagrammatically in Figure 33.

The catalyst (26.6 g, containing 6.7 g Co) was reduced in the synthesis reactor by passing dry electrolytic hydrogen downward at a rate of approximately 560 l per hr (hourly space velocity 5,600) for 2 hr at a temperature of 390°–405°C. At the end of this period, the catalyst was allowed to cool to 150°C in a slow stream of hydrogen. The catalyst was inducted with $2H_2 + 1CO$ synthesis gas, containing 6 per cent of inert constituents, passed at a throughput of 1 l per g Co per hr for 12 hr, while the temperature was raised from 150° to 175°C and for an additional 24 hr at 175°C. The temperature was raised to 180°C for the second 24-hr period and was then increased to 185°C (gas contraction 70–80 per cent) for the synthesis at atmospheric pressure. During the

test, temperatures were raised to maintain the yield at a value above 110 g C_5+ hydrocarbon products per cu m feed gas. For the entire test, the average yield was 122 g per cu m feed gas. In the first 3 weeks of operation, an average yield of 130 g per cu m was obtained at a substantially constant reaction temperature and without any reactivation treatment. The average composition of the total C_5+ products is shown in Table 43, together with data published by Martin of the Ruhrchemie A.G.[94] for products obtained in the cobalt synthesis at atmospheric pressure. Data for the total hydrocarbon product are also included.

Table 43. Comparison of British and German Data for Composition of Product from Cobalt Atmospheric-Pressure Synthesis

Fraction of Hydrocarbons	Per Cent by Weight			
	British [a]		German	
	Total	C_5+	Total	C_5+
$C_1 + C_2$	16	..	18	..
$C_3 + C_4$	7	..	11	..
C_5–200°C	49	64	43	61
200°–300°C	20	26	20	28
Residue (wax)	8	10	8	11
Total	100	100	100	100

[a] At average temperature of 190°C.

Comparison shows that less gaseous hydrocarbons and more low-boiling liquid hydrocarbons were produced than in the German commercial units.

Figure 34 shows the course of the experiment with respect to variations in temperature and average yield. The interruptions in the temperature record indicate the points at which hydrogen treatment was performed at 195°C for periods of 8 hr each. The major breaks in both curves, indicated by RR_1, RR_2, RR_3, and RR_4, represent the points at which rereduction with hydrogen was done at 400°C or above and a space velocity of dry hydrogen of 6,000, for 2 hr. The effect of the method of reactivation with hydrogen at low temperature upon the catalyst life is shown by the data in Table 44. Owing to the fact that in the last 28 days of section 4 a lower yield was tolerated than in earlier sections, the data for the first 100 days of this section are shown in the table separately as section 4*a*. In considering the results of this run in relation to large-scale practice, it is obvious that it would be necessary to remove the

[94] F. Martin, *Chem. Fabrik*, **12**, 233 (1939).

catalyst from the reaction vessel for rereduction treatment at 400°–450°C. Hence, the period between rereduction treatments would be the "converter life," and the period up to the point at which remanufacture of the catalyst was necessary would be the "total life." From

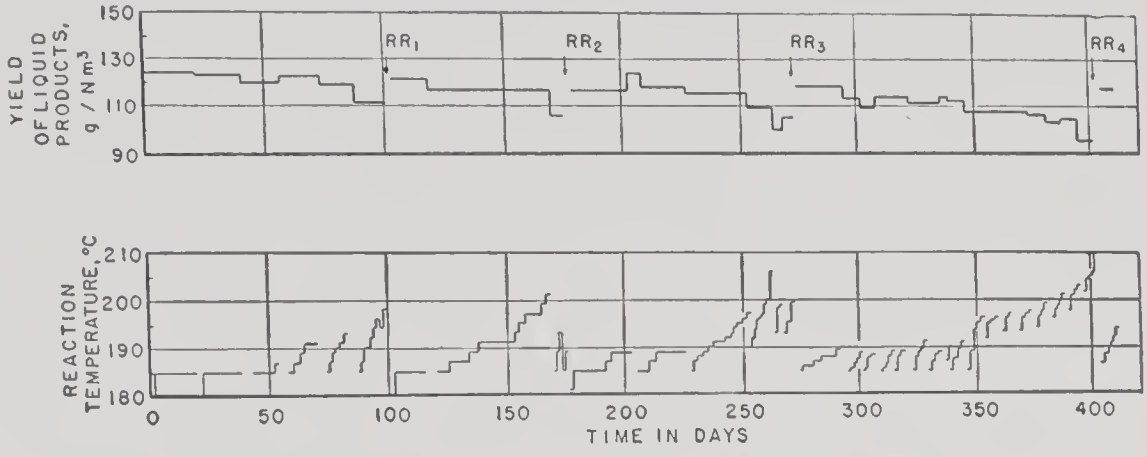


FIGURE 3-34. Durability test of $100Co:6ThO_2:3MgO:200$ kieselguhr catalyst at atmospheric pressure of $2H_2 + 1CO$ gas (British Fuel Research Station). Reproduced by permission from reference 93.

the results shown in Table 44, it was fairly clear that hydrogen dewaxing at short regular intervals, which permitted synthesis at the lowest possible reaction temperature (procedure used in section 4), gave the maximum converter life for a given output of liquid products. Further,

TABLE 44. EFFECT OF REACTIVATION WITH HYDROGEN UPON LIFE OF COBALT CATALYST (BRITISH FUEL RESEARCH STATION)

Section of Test	Duration, days	Number of Hydrogen Treatments	Average Yield, g per cu m feed gas
1. Start to RR_1	100	5	120
2. RR_1 to RR_2	75	2	117
3. RR_2 to RR_3	96	6	115
4. RR_3 to RR_4	128	16	110
4*a*. (RR_3 to 374th day)	100	12	112

operation without hydrogen treatment until the maximum useful reaction temperature of 200°C was reached (procedure used in last 60 days of section 2) gave the shortest converter life. The procedure found to be most effective for revivification of the catalyst was the following: passage of hydrogen every seventh day for 1–2 hr at a temperature 20°–25°C higher than the preceding synthesis temperature.

As a result of their study of the effect of hydrogen treatment upon the life of the cobalt catalyst in atmospheric-pressure synthesis, Hall and

Smith [93] believed that three processes caused the catalyst to become inactive, in addition to poisoning by sulfur compounds in synthesis gas. These were: (1) the relatively rapid deposition on the catalyst of hydrocarbons which can be readily removed by treatment with hydrogen; (2) a slower change, possibly oxidation of the cobalt, which can be reversed by repetition of the original reduction procedure; (3) a still more gradual but more fundamental change, probably a physical alteration of the active surface of the catalyst, which can be overcome only by remanufacture of the catalyst.

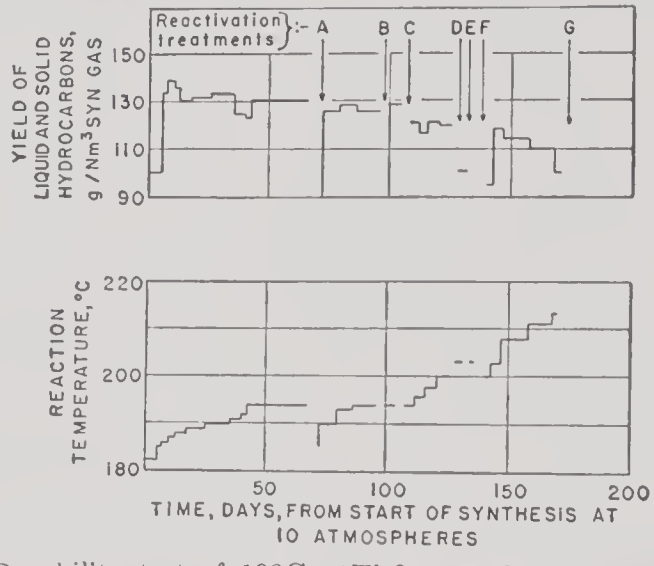


FIGURE 3–35. Durability test of $100Co:6ThO_2:3MgO:200$ kieselguhr catalyst at 10 atm pressure of $2H_2 + 1CO$ gas (British Fuel Research Station). Reproduced by permission from reference 95.

The course of a 6-month experiment at 10 atm with the same catalyst ($100Co:6ThO_2:3MgO:200$ kieselguhr) is shown graphically in Figure 35.[95] The catalyst was prepared and reduced in the manner described above and tested in an apparatus similar in design and dimensions to that shown in Figure 33, slightly modified for operation at pressures higher than atmospheric. Column I, Table 45, shows the more important data. For the first 130 days, the catalyst produced yields over 120 g C_5+ hydrocarbon product per cu m of feed gas and required only mild reactivation with hydrogen. Subsequently, neither more vigorous hydrogen treatment nor extraction with solvent (period *G*) was successful in restoring the full activity of the catalyst. Thus, it is apparent that the catalyst life was shorter at 10 atm than at atmospheric pressure. The composition of the combined liquid and solid reaction products at selected stages of the experiment is summarized in columns 2–7 of Table 46. A substantial increase in the proportion of wax over that produced

[95] C. C. Hall and S. L. Smith, *J. Inst. Petroleum*, **33**, 439–59 (1947).

TABLE 45. COBALT CATALYST TESTS AT 10 ATM OF $2H_2 + 100$ GAS [a]
(BRITISH FUEL RESEARCH STATION)

Synthesis Time, days	I: 100Co:6ThO_2:3MgO:200 Kieselguhr [b,c] Temperature, °C	I: Yield, g per cu m	II: 100Co:6ThO_2:3MgO:250 Kieselguhr [c,f] Temperature, °C	II: Yield g per cu m [d]
5 [e]	182	121	...	...
9	...	...	183	136
13	185	134	...	...
16	186	139	185	140
18	187	136	...	...
22	...	...	185	125
31	189	132	...	...
33	...	...	188	130
37	...	...	191	134
45	191	125	...	...
53	...	...	192	133
58	...	...	193	140 [g]
65	...	...	194	115
69	...	...	195	137 [g]
74	194	130	195	91
	A. H_2, 17 hr, 200°C, 10 atm, 14 l per hr		*J*. H_2, 8 hr, 205°C, 30 atm, 14 l per hr	
77	185	91	...	...
78	...	...	195	106
84	190	125	...	...
85	...	...	195	81 [h]
			L. H_2, 16 hr, 205°C, atmospheric pressure, 14 l per hr	
			M. H_2, 16 hr, 205°C, 0.1 atm, 14 l per hr	
90	...	...	197	71 [h]
			N. H_2, 16 hr, 207°C, atmospheric pressure, 14 l per hr 0–500 cc, 150°–200°C fraction, 150°C	
91	193	129	...	...
97	...	...	201	76 [h]
102	194	126		
	B. H_2, 2 hr, 194°C, 10 atm, 560 l per hr			
110	194	129		
	C. H_2, 8 hr, 210°C, 10 atm, 14 l per hr			
117	194	120		
126	198	121		
132	200	120		
	D. N_2, 6 hr, 220°C, 10 atm, 14 l per hr			
137	203	102		
	E. H_2, 6 hr, 220°C, 10 atm, 14 l per hr			
140	203	113		
	F. H_2, 19 hr, 220°C, 10 atm, 14 l per hr H_2, 2 hr, 400°C, atmospheric pressure, 560 l per hr			
154	203	118		
163	208	114		
176	213	100		
	G. 500 cc, 170°–240°C, fraction at 150°C			
180	212	60		
	H. H_2, 16 hr, 230°C H_2, 2 hr, 400°C, 10 atm, 14 l per hr			
184	213	82		
	I. H_2, 2 hr, 400°C, atmospheric pressure Steam, 3.5 hr, 350°–400°C H_2, 2 hr, 400°C, atmospheric pressure			
192	213	74		

[a] Composition, 31.5 per cent CO, 62.0 per cent H_2, 2.5 per cent CO_2, and 4.0 per cent N_2.
[b] 100 cc catalyst = 26.7 g = 6.7 g Co.
[c] Throughput = 1 l (NTP) per g Co per hour.
[d] Grams per cubic meter feed gas.
[e] At atmospheric pressure.
[f] 100 cc catalyst = 41.8 g = 9.4 g Co.
[g] Throughput = 0.5 l (NTP) per g Co per hour.
[h] These low yields probably resulted because insufficient time elapsed for the catalyst to become saturated with wax. The gas contraction, 57, 60, 64 per cent respectively, in these cases, was the more reliable guide to the catalyst activity.

at atmospheric pressure and a decrease in the proportion of light oil and olefins were evident.

Another catalyst, of which the composition was $100Co:6ThO_2:3MgO:250$ kieselguhr, was prepared by the procedure described above, but in a batch of 3 kg on a pilot-plant scale. The kieselguhr used in this preparation had the property of increasing the bulk density of the catalyst, so that, in spite of the increased proportion of kieselguhr, 100 cc of the unreduced catalyst granules weighed 41.8 g and contained 9.4 g cobalt.

TABLE 46. PRODUCT DISTRIBUTION FROM COBALT SYNTHESIS AT 10 ATM OF $2H_2 + 1CO$ GAS (BRITISH FUEL RESEARCH STATION)

Catalyst	$100Co:6ThO_2:3MgO:200$ Kieselguhr						$100Co:6ThO_2:3MgO:250$ Kieselguhr				
1	2	3	4	5	6	7	8	9	10	11	12
Period of test, days	6–18	41–52	59–70	85–102	127–132	149–159	34–37, 41–44	38–40	45–47, 52–53	48–51 [a]	54–58, 66–69
Synthesis temperature, °C	185	192	194	194	200	204	191–195	192	192–195	193	194
Space velocity, l per g Co per hr	1	1	1	1	1	1	1	1.5	1	1	0.5
Distribution of C_5+ product, per cent by weight (olefins, per cent by weight)											
<150°C	29.0 (16.0)	21.7 (14.0)	18.6 (18.0)	14.9 (14.0)	13.2 (14.0)	18.6 (6.0)	23.0 (12.1)	33.3 (14.3)	24.6 (11.7)	36.7 (12.6)	19.4 (5.2)
150°–200°C	13.0	12.4	10.1	10.2	10.7	11.9	13.2	14.8 (7.0)	12.8	14.8	13.1
200°–300°C	22.2	24.5	25.1	23.7	24.6	30.8	27.2	28.8	22.6	21.2	22.1
>300°C	35.8	41.4	46.2	51.2	51.5	38.8	36.6	23.1	40.0	27.3	48.4

[a] 30 per cent N_2 added to synthesis gas, gas rate = 1 l normal synthesis gas per g Co per hr.

As the data in column II of Table 45 and columns 8–12 of Table 46 show, the performance of this catalyst at 10 atm during the first 50 days was similar to that in column I, despite the fact that the gas throughput in this experiment was 40 per cent higher. Subsequent lowering of the space velocity caused premature and permanent deactivation of the catalyst. The conclusion drawn from the reactivation attempts was that hydrogen treatment was necessary at or above the synthesis pressure; catalyst improvement was, however, small compared with that obtained by such treatment in the atmospheric-pressure synthesis. Removal of wax by reaction with hydrogen was favored by reduction in pressure.

Roelen [29,35] stated that in Germany wax was removed from the catalyst on the large scale by a combination of treatments: *ie*, hydrogenation at synthesis temperature and extraction with solvents. The former treatment reduced the wax content to 2–5 per cent; and the latter, to 1–2 per cent. However, it was generally agreed that the best revivification was achieved by extracting the catalyst with solvent and then treating it with hydrogen.

Hydrogen revivification was done on the commercial scale with a space velocity of 1,000 cu m per reactor per hr and was continued for 7–10 hr at a temperature 5° higher than the last synthesis temperature (Ruhrchemie) or always at 200°C (Essener Steinkohle). Ruhrchemie specified pure hydrogen; Rheinpreussen indicated that a little carbon monoxide in the hydrogen had no bad effect; Essener Steinkohle used only 86 per cent hydrogen. The composition of the products obtained by the hydrogen treatment depended upon the amount of hydrogen used. Normally, 50–60 per cent consisted of methane, and the remainder, of saturated hydrocarbons boiling below 200°C.

At Ruhrchemie and Brabag, the procedure for solvent extraction consisted in spraying into the reactor oil boiling in the Diesel oil range. Essener Steinkohle, which regarded solvent extraction as the milder treatment and used this alone during the first part of the catalyst life, used a continuous extraction method.[29] Oil was distilled into the top of the reactor, and the solution of wax was removed at the bottom in a small portable still. Here it was redistilled and the oil vapor reintroduced into the top of the reactor. The temperature during extraction was kept at 100°C, and the process was continued until no more wax was removed. For a block of four reactors about 60 cu m of oil was in circulation. The boiling range of the oil used was 80°–200°C, the major fraction of it boiling between 180° and 200°C. Only when the catalyst ceased to respond to such treatment was the more vigorous combined treatment used.

Table 47 [29] illustrates the reactivation of the catalyst and the recovery of catalyst wax on a commercial scale. The data were obtained at the Essener Steinkohle plant in 1944 from a block of four reactors operated at atmospheric pressure of $2H_2 + 1CO$ in stage 1 from the 106th to the 277th day, during which time the synthesis temperature was raised from 185° to 196°C. Although the normal practice was to follow the extraction immediately by the hydrogen treatment, in this operation a few days of synthesis was done between the two treatments to determine how far the activity was restored by the solvent alone. The temperatures recorded in Table 47 show that the solvent treatment became less and less effective; on the 215th day, the synthesis temperature after extraction was only 1.8°C lower than before extraction. After

hydrogenation, the temperature on the 219th day was 13.9°C lower than before hydrogenation. Subsequently, hydrogen treatment also became less effective.

TABLE 47. REVIVIFICATION OF CATALYST AND RECOVERY OF CATALYST WAX FROM ONE BLOCK OF FOUR REACTORS, STAGE 1, ATMOSPHERIC SYNTHESIS OVER Co CATALYST, ESSENER STEINKOHLE, 1944

Cumulative Time, days	Synthesis Temperature, °C	Synthesis Gas Throughput, cu m per hr	Removal of Wax	
			Treatment [a]	Quantity, kg
106	185.5	980	..	.....
113	190.5	980	S	9,310
114	182.5	1,070	..	.....
134	191.8	1,020	S	8,830
135	185.5	1,050	..	.....
160	193.0	960	S	6,380
161	184.0	960	..	.....
177	194.0	1,050	S	2,560
178	188.0	960	..	.....
196	195.0	1,030	S	2,450
197	192.8	1,040	..	.....
214	195.5	1,050	S	2,270
215	193.7	1,100	..	.....
218	195.2	1,100	H	.....
219	181.3	1,050	..	.....
232	195.0	1,070	S	5,400
233	191.5	920	..	.....
238	193.2	900	H	.....
239	180.5	1,070	..	.....
251	195.5	1,090	S	3,130
252	194.5	940	..	.....
253	186.0	1,000	H	.....
273	197.3	870	..	.....
274	194.1	900	H	.....
277	195.5	1,020	S	640
	Total	40,970		
	Per cent of Co	1,024		

[a] S = solvent extraction; H = 86 per cent hydrogen treatment.

The quantity of catalyst wax collected after each solvent extraction was smaller than each previous recovery. The first solvent extraction on the 232nd day, following the first hydrogen treatment, produced a noticeable increase in catalyst wax, which quickly tapered off. Probably the explanation of these results is that solvent extraction removed lower-molecular-weight hydrocarbons, while higher-molecular-weight hydrocarbons accumulated on the catalyst. Removal of the latter by hydro-

genation left a large portion of catalyst pores free for further accumulation of wax. A total quantity of 40,970 kg of wax was removed from the catalyst. Since each reactor contained about 3,000 kg of catalyst of which 1,000 kg was cobalt, simple calculations show a production of 3.4 g of wax per g of catalyst and 10.2 g per g of cobalt.

At the end of 6–8 months, catalysts could no longer be reactivated by solvent or hydrogen treatment, as described above, because the wax and other organic material were no longer being removed. Ruhrchemie [29] found that such catalysts could be reactivated by "dry regeneration," which was a rereduction with a high space velocity of $75H_2$-$25N_2$ at 200°C for 1.5 hr, followed by an increase in temperature to 450°C during a period of 2 hr and further reduction at 450°C for 2 hr. The effectiveness of this treatment is indicated by the following example: A catalyst of composition $100Co:5ThO_2:10MgO:200$ kieselguhr, which had been used for synthesis for 500 hr at 185°C, contained 320 g of deposit per 100 g of cobalt. Dry regeneration resulted in the removal and recovery of 315 g of material, as follows:

CH_4 and higher hydrocarbons	181.0
CO_2	2.6
CO	1.4
Wax	130.0

Fifty per cent of the cobalt was present as metal before this treatment; afterwards, 75–80 per cent. Dry regeneration was, however, not practiced on the full scale by Ruhrchemie for two reasons. The first was a shortage of hydrogen, because the methane produced precluded the recirculation of the hydrogen; the second was that after dry regeneration the catalyst required screening in an atmosphere of carbon dioxide, which was not feasible owing to a lack of suitable equipment.

Iron Catalysts

HISTORICAL CONSIDERATIONS

Although the cobalt catalyst became the German commercial catalyst because its development occurred more quickly than that of the iron catalysts, research on iron catalysts in the laboratory and pilot plants was continuously being done and is still in progress. An important advantage of iron over cobalt is that it imparts great flexibility to the Fischer-Tropsch process. By variation in catalyst composition, method of preparation, method of reduction, composition of synthesis gas, and process conditions, the course of the reaction can be regulated for the

production of a large fraction of wax, or gasoline, or olefins, or alcohols. In addition, iron is easily available from many sources, whereas the supply of cobalt is limited.

The best iron catalyst developed by Fischer up to 1930 was an alkalized iron-copper preparation made by decomposition of the nitrates and tested at atmospheric pressure in the laboratory at the Kaiser Wilhelm Institut für Kohlenforschung. When an iron-copper catalyst was operated with water gas at atmospheric pressure and about 250°C, the fraction of the oil product boiling in the range 60°–185°C was 70 per cent olefinic and contained pentene-1, pentene-2, hexene-1, hexene-2, heptene, octene-2, and a very small amount of 3,3-dimethylpentene-1.[96] The 30 per cent of saturates contained pentane, hexane, heptane, octane, nonane, and isononane. The isononane was probably 3-methyloctane and was present in very small amount. No diolefins or naphthenes were found. Minute amounts (0.1–0.4 per cent) of benzol and toluol were present. Despite the high olefin content, the gasoline was only pale yellow. Paraffin obtained by recrystallization from acetone was colorless and odorless and solidified at 61°C. Production of higher-molecular-weight paraffin (molecular weight about 1,000) was observed when alkalized iron-copper catalyst was operated at 10–15 atm of water gas at 280°C.[96] This paraffin melted in the range 104°–117°C and solidified at 109°C.

Unfortunately, most of the tests made at this time were carried out at atmospheric pressure, and significant improvement in the development of iron catalysts was not observed until a decade later. During this period tests of numerous iron-copper and alkalized iron-copper catalysts prepared by decomposition or by precipitation and operated at atmospheric pressure were reported by German,[18] American,[97] and Japanese [98–100] investigators. For example, an iron-copper (4:1) catalyst was precipitated by sodium hydroxide from a hot solution of ferric and cupric nitrates.[97] It was washed by decantation until it began to become colloidal and was molded by being forced through a grease gun in a semi-soft state. After slow drying in air up to 200°C, the catalyst granules were slowly reduced in the converter first by a hydrogen-nitrogen mixture at 150°C and then by a gradually increasing temperature and concentration of hydrogen until pure hydrogen was used at 285°C. In syn-

[96] F. Fischer and H. Tropsch, *Ber.*, **60**, 1,330–4 (1927).

[97] D. F. Smith, C. O. Hawk, and P. L. Golden, *J. Am. Chem. Soc.*, **52**, 3,221–33 (1930).

[98] K. Fujimura, *J. Soc. Chem. Ind. Japan*, **34**, Suppl. Binding, 136–8 (1931).

[99] S. Kodama, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **14**, 169–83 (1930).

[100] S. Kodama and K. Fujimura, *J. Soc. Chem. Ind. Japan*, **34**, Suppl. Binding, 14–6 (1931).

thesis at 261°C and a space velocity of 360 (volumes of gas per volume of catalyst space per hour), the average yield of C_5+ hydrocarbons was 31 g per cu m of water gas charged. The methane fraction was very small. Iron-copper-manganese oxide, prepared by the same procedure, was similar in activity and physical properties.

The maximum yield from an iron-copper-manganese catalyst deposited on silica gel and containing 0.4 per cent potassium carbonate was 30–35 g per cu m synthesis gas containing $1CO + 2H_2$ (corresponding to 40–45 g per cu m $CO-H_2$ mixture).[18] The maximum yield from an iron-copper catalyst precipitated on kieselguhr was 28 g. The life of these catalysts, when tested at atmospheric pressure, was 8 days. Fischer and Meyer,[101] in experiments in 1934–1936, produced yields of 50–60 g per cu m of synthesis gas containing $2H_2 + 1CO$ from iron (Fe^{+2})-copper precipitated catalysts tested at atmospheric pressure. The catalyst life was 4–6 weeks. In 1936, Fischer and Ackermann [102,103] obtained 55 g of liquid hydrocarbons per cu m of synthesis gas from copper-free iron catalysts operated at atmospheric pressure. Within 3 weeks the yield decreased by 20 per cent. In 1937, a precipitated iron catalyst that had been under test for several weeks by Fischer and Pichler was put under 15 atm.[32] The yield was almost doubled, and the life of the catalyst was increased several fold. The following sections will describe the various lines of development of iron catalysts which occurred in the ensuing decade.

EFFECT OF ALKALI UPON ACTIVITY AND PRODUCTIVITY

The effect of alkali in producing higher-molecular-weight products had been observed when the synthol process was discovered. Addition of alkali to Fischer-Tropsch iron catalysts constituted one of the most important steps in their development.

[101] T.O.M. Reel 101, Doc. PG-21,581-NID, Recent Investigations on Iron Catalysts. Translation in *Translations of German Documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis*, Part I, M. Leva, *U. S. Bur. Mines Rept.*, Pittsburgh, Pa., 1946, pp 68–158.

[102] T.O.M. Reel 101, Doc. PG-21,559-NID, Report on the Middle-Pressure Synthesis with Iron Catalysts, June 1940; T.O.M. Reel 101, Doc. PG-21,574-NID, Iron Catalysts for the Middle-Pressure Synthesis, Lecture by H. Pichler, Sept. 9, 1940. Translations of these two reports in *Translations of German Documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis*, Part I, M. Leva, *U. S. Bur. Mines Rept.*, Pittsburgh, Pa., 1946, pp 1–67.

[103] T.O.M. Reel 101, Doc. PG-21,578-NID, The Middle-Pressure Synthesis with Iron Catalysts, Sept. 9, 1939. Translation in *Translations of German Documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis*, Part II, M. Leva and H. V. Atwell, *U. S. Bur. Mines Rept.*, Pittsburgh, Pa., 1946, pp 11–21.

One of the earliest studies on this subject was made by Fischer.[5] He had observed that a powdered iron-copper (4:1) catalyst prepared by decomposition and ignition of the metal nitrates produced very small quantities of hydrocarbon products at atmospheric pressure and temperatures between 260° and 270°C. When 0.5 per cent potassium carbonate (based on weight of Fe-Cu oxides) was added to the oxide mixture, yields of 25–30 g of C_5+ hydrocarbons (including solid paraffin) were obtained, per cu m of water gas, at 250°C. Addition of the alkali either dry or as a paste produced the same results. After reactivation with air at the end of 100 hr, the productivity was maintained during an additional 100 hr.

As shown in Figure 36, about 0.3 per cent of potassium carbonate was the optimum amount of alkali. Tests were made at 250°C with 20 g

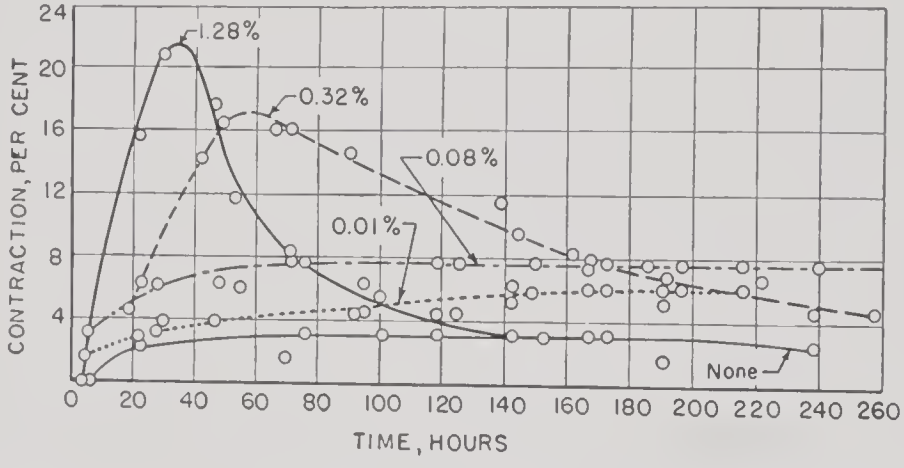


FIGURE 3–36. Effect of amount of added K_2CO_3 on activity of 4 g of Fe-Cu (4:1) catalyst. Reproduced from reference 5.

of oxide mixture (15-cm layer) and a flow of 4 l per hr of water gas. Amounts smaller than 0.3 per cent slowly activated the catalyst to a state that was maintained for about 200 hr. More than 1 per cent of potassium carbonate caused an immediate, sharp rise in activity, which decreased after only 40 hr. Kodama and Fujimura [104] observed similarly that an iron-copper (1:1) catalyst containing about 0.5 per cent of alkali was active for a considerably longer time than those containing more alkali.

When the source of potassium was KF, KI, K_2SiF_6, K_2HPO_4, $KAsO_2$, or potassium pyroantimonate, and was added in amounts corresponding to the equivalent quantities of K_2CO_3, a similar activating effect was observed.[5] It is interesting to note in several patents issued in 1948 and

[104] S. Kodama and K. Fujimura, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **29**, 272–9 (1936).

1949 a report of the recent discovery of the activating effect of 0.2–20 per cent alkali pyroantimonate and 5 per cent potassium ferrate, K_2FeO_4.[105] Potassium sulfate exhibited a poisoning effect upon the catalyst.[5] Discussion of the effect of sulfur is presented in a later section of this chapter, p 312. Although chlorine as potassium chloride had little effect upon the activity of the catalyst and did not inhibit the activating effect of potassium carbonate, chlorine bound to iron under certain conditions retarded or destroyed its activity. In the U. S. Bureau of Mines laboratory this phenomenon was the subject of an investigation, which is described on p 255 of this chapter.

One-half per cent (by weight of metal oxides) of the carbonates of other alkalis, lithium, sodium, rubidium, calcium, and barium was added dry to powdered iron-copper (4:1) catalyst, to compare the effect of other alkalis with that of potassium. The results shown in Table 48 and

TABLE 48. EFFECT OF ALKALI UPON ACTIVITY OF Fe-Cu (4:1) CATALYST

(4 g catalyst in a layer 5 cm long, tested at 250°C at a flow of 4 l per hr of water gas.)

Alkali Added, 0.5 Per Cent as Carbonate	Conditions at Maximum Contraction			First Operating (70-hr) Period			
	Maximum Contraction, per cent	Time, hr	CO_2 in Product Gas, per cent	Contraction, per cent	CO_2 in Product Gas, per cent	C_5+ Hydrocarbons, g per cu m [a]	
K	26.5	11	...	5.2	6.4	1.58	5.6
Rb	23.5	11.5	...	4.5	4.8	1.20	4.3
Na	10.3	21	9.1	7.5	7.2	0.30	1.1
Ba	10.4	22	9.2	7.4	7.8	0.23	0.8
Ca	10.2	21	9.4	6.6	6.8	0.18	0.6
None	7.4	24	7.2	6.2	5.3	0.11	0.4
Li	6.0	22	6.4	4.6	4.0	0.11	0.4

[a] Per cubic meter of $1H_2 + 1CO$.

Figure 37 were obtained in a 70-hr period from 4 g of catalyst tested in a layer 5 cm long at 250°C and at a flow of 4 l per hr of water gas at atmospheric pressure.[5] The potassium- and rubidium-containing cata-

[105] M. A. Mosesman (to Standard Oil Development), U. S. Patents 2,438,449, Mar. 23, 1948; 2,454,398, Nov. 23, 1948; 2,455,696, Dec. 7, 1948; 2,470,784, May 24, 1949.

lysts produced the highest yields of liquid and solid hydrocarbons, the distribution of products being strongly shifted toward solids. Calcium-, barium-, and sodium-containing catalysts showed lower activity, which tapered off less sharply than that of the first two catalysts. The sodium-containing catalyst produced more liquid hydrocarbons than the potassium catalyst. Lithium produced a poorer catalyst than no alkali.

Because the German objective before World War II was the production of hydrocarbons in the gasoline and Diesel oil ranges, the observation that the addition of sodium favored the production of liquid rather

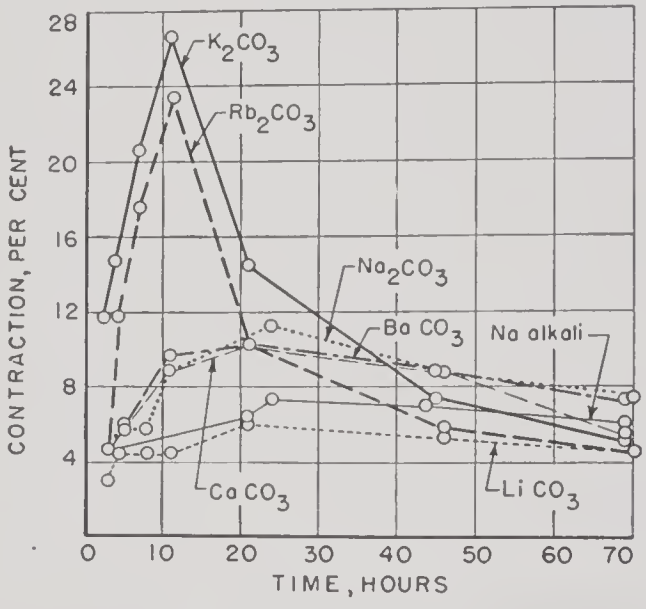


FIGURE 3–37. Effect of adding 0.5 per cent alkali on activity of 4 g of Fe-Cu (4:1) catalyst. Reproduced from reference 5.

than solid hydrocarbons was of interest. Tests were made with catalysts containing other sodium compounds, such as sodium glass powder and sodium aluminate.

Powdered iron-copper (1:1) catalyst was mixed with 10 per cent of glass powder, obtained by finely pulverizing soft laboratory glass tubes, and tested at atmospheric pressure in a 20-cm layer (40 g) with a flow velocity of 4 l of water gas per hr, without preliminary reduction. In the first 24 hr of the test at 270°C, the catalyst produced 7 times as much liquid hydrocarbons as a control catalyst containing no glass powder. After reactivation, the glass-powder catalyst showed increased activity at 250°C; the control catalyst was virtually inactive. The results of several additional operating periods at 245°C, separated by periods of reactivation with air, are shown in Table 49.[5] The highest yield was 47.2 g of C_5+ hydrocarbons, per cu m of $1H_2 + 1CO$, obtained after 168 hr of operation. The whole test lasted about 1,000 hr. A comparable catalyst

richer in iron (Fe:Cu = 4:1) produced 15.4 g of methane, 63.8 g of C_1–C_4, and 34.1 g of C_5+ hydrocarbons per cu m of $1H_2 + 1CO$ gas, in the first 24 hr at 250°C. A shift in distribution of products toward lighter hydrocarbons was observed. More gaseous hydrocarbons and less higher-boiling oil were produced; the yield of hydrocarbons in the gasoline range was the same.

TABLE 49. EFFECT OF ADDITION OF 10 PER CENT SODIUM GLASS POWDER TO Fe-Cu (1:1) POWDERED CATALYST

[Atmospheric-pressure test of 40 g catalyst (20-cm layer), using a flow velocity of 4 l per hr of water gas.]

Cumulative Time, hr	Temperature, °C	Contraction, per cent	Hydrocarbons, g per cu m $1H_2 + 1CO$		
			CH_4	C_1–C_4	C_5+
24	270	31.7	14.8	55.3	34.9
96	250	32.5	11.2	52.0	36.8
168	245	29.0	7.6	43.9	47.2
288	245	34.2	10.1	53.7	46.7
480	245	33.2	13.2	61.7	35.4
480–636	245	31.1	....	....	23.5
780	245	24.9	14.9	46.6	10.1
798	245	30.2	9.0	43.6	43.6
798–983	245	34.0	....	....	28.9

Addition of larger quantities of glass powder did not further increase activity but did decrease the life of the catalyst. For example, a catalyst containing equal parts of iron-copper (4:1) oxide and glass powder gave a maximum contraction of 38.5 per cent in 29 hr, which decreased to 14 per cent in 67 hr. Removal of soluble alkali by digesting glass powder with nitric acid before adding it to the catalyst produced little effect upon the activity of the catalyst. An iron-copper (4:1) catalyst containing 10 per cent of acid-treated glass powder produced a maximum contraction of 32.3 per cent and the following hydrocarbon products, in grams per cubic meter of water gas: methane 20.7, C_1–C_4 69.3, and C_5+ 35.8.

The effect of the addition of sodium aluminate upon a 20-cm layer of powdered iron-copper (4:1) catalyst tested at a flow velocity of 4 l per hr of water gas is shown in Table 50.[5] Aluminum hydroxide, obtained

by precipitation from the nitrate by ammonia, was mixed as a paste with varying amounts of sodium hydroxide solution and then was evaporated to dryness. A quantity of the product equivalent to 10 per cent of the catalyst oxides was added to the iron-copper mixture. One-third mole of sodium hydroxide per mole of aluminum hydroxide was the optimum amount to add. This was much less than the equivalent amount required to produce sodium aluminate, $Al(ONa)_3$. This catalyst was active over an 18-day period and produced almost 50 g of C_5+ hydrocarbons per cu m of water gas at a low temperature of 230°C.

TABLE 50. EFFECT OF SODIUM ALUMINATE UPON AN IRON CATALYST [Fe-Cu (4:1) + 10 PER CENT $Al(OH)_3$]

(Atmospheric-pressure test of a 20-cm layer at a flow velocity of 4 l per hr water gas.)

NaOH [a] Added, mole	Time, days	Temperature, °C	Contraction, per cent	Hydrocarbons, g per cu m water gas		
				CH_4	C_1-C_4	C_5+
1	..	230	....	6.3	46.9	26.2
$\frac{1}{15}$	..	240	....	15.4	60.3	22.8
$\frac{1}{3}$	..	240	....	14.8	62.7	40.1
$\frac{1}{3}$	4	230	28.0	5.7	38.0	26.2
$\frac{1}{3}$	5	230	31.4	7.1	36.6	48.1
$\frac{1}{3}$	10	230	32.2	10.0	42.6	49.6
$\frac{1}{3}$	14	230	33.2	11.3	48.5	40.8

[a] Per mole of $Al(OH)_3$.

When 10 per cent aluminum hydroxide was added to an iron-copper (4:1) catalyst previously activated by dry admixture of 0.5 per cent potassium carbonate, based on iron-copper oxides, the production of solid paraffin was retarded. In a test at 250°C small amounts of paraffin appeared in 96 hr; in a similar test with an $Al(OH)_3$-free catalyst, paraffin was observed within 21 hr. In a test at 240°C, the oil was colorless until the 300th hr, then became increasingly yellow. Very little solid paraffin was observed until the 200th hr in this test.

Pichler [32,102] reported that during 2 months of synthesis two precipitated iron catalysts containing 0 and 0.25 per cent of added K_2CO_3, based on iron, respectively, showed similar activity when tested at 15 atm of $3CO + 2H_2$ and 235°C. Catalysts containing more than 1 per cent of K_2CO_3 were less active than that containing 0.25 per cent, as

shown by lower gas contractions (Table 51). The more rapid production of elemental carbon in the more highly alkalized catalysts probably accounted for their shorter life. As previously observed by Fischer,[5] not only the carbonate but also other potassium salts could be used to furnish the potassium.

TABLE 51. EFFECT OF ALKALI CONTENT OF PRECIPITATED IRON CATALYSTS UPON YIELD AND DISTRIBUTION OF HYDROCARBON PRODUCTS IN MEDIUM-PRESSURE SYNTHESIS

(235°C and 15 atm of $3CO + 2H_2$ gas containing 8–10 per cent inerts.)

Alkali		Contraction, per cent													Hydrocarbon Products			
		After Time Intervals, days													Yield C_2+, g per cu m [a]	Distribution, weight per cent		
Compound	Per Cent of Fe	1	2	5	6	8	9	10	20	30	40	50	60	100		C_2-C_4	Liquid	Wax [b]
None [c]	.....	50	50	50	..	..	..	50	50	49	51	51	..	..	141	21	67	12
None	.....	53	50	48	..	..	..	49	.	..	.	..	..	..	140	28	67	13
K_2CO_3	0.25	47	50	50	..	..	..	51	55	56	54	54	..	53	148	18	56	26
K_2CO_3	0.5	54	..	54	..	..	..	47	.	45	.	..	..	..	...	.	.	.
K_2CO_3	1	45	45	45	..	..	..	52	48	48	47	..	..	.	157	11	47	42
K_2CO_3	2	45	45	47	..	..	..	46	47	50	..	..	..	..	143	13	44	43
K_2CO_3	5	..	..	45	..	..	..	50	50	51	50	40	..	..	158	11	44	45
K_2CO_3	10	..	50	47	..	..	..	50	45	42	..	..	..	..			..	.
$KMnO_4$	1	40	..	50	..	..	..	51	55	50	..	..	..	..	155	14	45	41
K_2F_2	1	..	57	53	..	..	..	55	48	..	..	..	..	.	163	12	42	46
K_2SiO_3	1	..	54	53	..	..	..	46	50	..	..	..	..	..	158	16	41	43
K_2HPO_4	1	55	46	..	..	..	..	46	40	..	..	..	..	..	154	10	52	38

[a] Grams per cubic meters $3CO + 2H_2$. Average of first month.

[b] Determined by butanone method.

[c] This catalyst was precipitated by NH_4OH, all others by Na_2CO_3.

The data presented in Table 51 also show the increased production of paraffin wax with increasing alkali content of the catalyst. The increase was sharper at 0.25 and 1 per cent of added K_2CO_3 than at 2 and 5 per cent of added K_2CO_3. The properties of the paraffin wax produced by a catalyst containing 1 per cent of K_2CO_3 are shown in Table 52. When a CO-rich gas, such as $3CO + 2H_2$, was used and the catalyst contained 1 or more per cent of K_2CO_3, the paraffin was yellow or yellow-brown; when a H_2-rich gas was used with a catalyst containing little or no alkali, the paraffin was white or pale yellow. Pichler's [102] data indicated also

Table 52. Some Properties of Wax Produced by Precipitated Iron Catalyst Containing 1 Per Cent of K_2CO_3 (Kaiser Wilhelm Institut)

Solvent	Weight Per Cent Soluble in Solvent [a]	Melting Point, °C
	Wax from oil	
Ether	50	66–70 [b]
Hexane	41	90–104
[c]	9	122
	Wax from catalyst	
Toluene	..	126

[a] Extraction in Soxhlet apparatus for 24 hr.
[b] Reprecipitated from methyl alcohol.
[c] Insoluble in ether and hexane.

that production of oxygenated constituents in the liquid hydrocarbon fractions was favored by alkalization. Table 53 shows acid, ester, saponification, and hydroxyl numbers of the product boiling over 180°C from two precipitated iron catalysts containing 0.25 and 1 per cent of K_2CO_3, respectively.

Table 53. Oxygenated Content of >180°C Fraction of Product from Alkalized Precipitated Iron Catalysts (Kaiser Wilhelm Institut)

K_2CO_3 Content, per cent of Fe	Acid Number	Ester Number	Saponification Number	Hydroxyl Number
0.25	0.2	0.2	0.5	2.3
1	1.8	8.1	9.9	7.0
1 [a]	0.1	2.0	2.1	...

[a] Catalyst contained 40 per cent of kieselguhr, based on iron.

The iron catalysts tested in 1938 and 1939 at Steinkohlenbergwerk Rheinpreussen Homberg contained iron chiefly in the ferric form and in addition about 0.2 per cent of copper and 0.25 per cent K_2CO_3 (based on iron). They were gasoline-producing catalysts [106] and were precipitated from commercial iron by sodium carbonate or ammonia. No copper was added in the preparation of these catalysts because earlier tests had indicated that small amounts (<0.5 per cent, based on iron) were present in catalysts precipitated from nitric acid solution of commercial iron. The catalysts were inducted with CO-H_2 mixtures at atmospheric pressure and about 250°C. Medium-pressure synthesis in the conventional gas-phase reactors was carried out at temperatures of

[106] F.I.A.T. Reel 115-X, Frames 1,181–261, 1938–9.

about 257°C with gas mixtures consisting of $2H_2 + 1CO$ and $2H_2 + 3CO$. The results obtained in two single-stage, 4-month tests of the sodium carbonate-precipitated, alkalized, standard iron catalyst operated at 10–15 atm are summarized in Table 54, columns *A* and *B*. Distribution of the C_5+ fraction from the test with $2H_2 + 3CO$ gas (column *B*) was as follows, in weight per cent: boiling range <200°C 65, 200°–320°C 19, and >320°C 16. The C_5 fraction constituted 20 per cent of the total liquid product, C_6 12–14 per cent, and C_7 10–12 per cent. Olefins comprised 70 per cent of the C_5 fraction. The gasol frac-

Table 54. Tests of Rheinpreussen Precipitated, Alkalized Iron Catalysts

Catalyst	*A*	*B*	*C*	*D*
Process phase	Gas	Gas	Liquid	Liquid
Time, days	120	120	.....	.....
Gas, H_2:CO	2	0.67	0.5	0.5
Space velocity	140	130	75 [a]	75 [a]
Pressure				
Atmospheres	10–15	12	10	8–10
Temperature, °C	257	257	250	230–245
CO conversion, per cent	90.2	91.4	.....	About 90
Use ratio, H_2:CO (*X*)	.....	.....	0.5	0.5
Yield, g per cu m of H_2 + CO				
$C_1 + C_2$	.....	.....	vs [b]	vs [b]
$C_3 + C_4$ (olefins, volume per cent)	32	37(65)	36	.....
C_5+ (olefins, volume per cent)	113	108(60)	132	.....
Total	.....	.....	168	142
Product distribution, per cent of CO converted				
CH_4	13.0	....	.....	.....
$C_3 + C_4$	19.2	....	.....	.....
C_5+	66.6	60.3	.....	.....
Product distribution, C_5+, weight per cent				
<200°C	.....	65(65) [c]	67.5(68.5) [c]	.....
200°–290°C	.....	19(72) [d]	25.5	.....
290°–320°C	.....			50–60
>320°C	.....	16	7	

[a] Volume of gas per volume of reaction space per hour, equivalent to 750 volumes gas per volume dry catalyst per hour.

[b] Very small.

[c] Motor octane number in parentheses.

[d] Cetane number in parentheses.

tion consisted of 60 per cent C_4 and 40 per cent C_3 hydrocarbons. When used in the medium-pressure liquid-phase synthesis the development of which is described in Chapter 4, the same catalyst produced less methane and larger oil fractions. Column *C* of Table 54 shows some performance data reported by Kölbel during an interview in 1947.[107] The fraction boiling below 200°C was the largest. The motor octane number for the fraction boiling below 150°C was 77; this fraction was 60 per cent olefinic.

When the Rheinpreussen catalyst contained 1 per cent K_2CO_3, high wax and increased alcohol production was observed. The catalyst used in most of the investigations in the liquid phase had the composition $100Fe:(0.2–0.5)Cu:1K_2CO_3$.[29,107] It was prepared by dissolving wrought iron in nitric acid to give a 5 per cent solution and adding 0.3 per cent (based on iron content) of copper as the nitrate.[108] The metal nitrate solution was heated to boiling and precipitated with boiling 20 per cent sodium carbonate solution until the reaction mixture was neutral (indicated by change in color of red litmus paper to violet). The precipitate was filtered, washed several times with a ten-fold quantity of water, calculated on iron content, impregnated with aqueous K_2CO_3, and dried at 110°C. It was then suspended in synthetic oil and ground in a ball mill to a particle size <0.1 mm in diameter.

Test data summarized in column *D* of Table 54 were obtained with this catalyst in one-stage synthesis in the liquid phase. A suspension containing 10–20 per cent iron was tested at 230°–245°C and 8–10 atm of $1H_2 + 2CO$ gas at an hourly space velocity of about 75. As high a proportion of wax as 67 per cent of the total product was possible, *ie*, 95 g when the total yield was 142 g per cu m of $1H_2 + 2CO$. It is possible that this wax had an initial boiling point of 290°C, but yields of wax of br >320°C (74 g in a total of 140 g per cu m, or 50 per cent) were not uncommon. The product contained 50–60 per cent olefins and 10–25 per cent alcohols.

When interrogated late in 1947, Kölbel [107] stated that recent minor modifications made in the catalyst resulted in increased gas utilization ratio ($H_2:CO$) and permitted the use of water gas or synthesis gas under suitable operating conditions. He did not reveal what the changes were, but admitted that no carrier had been incorporated.

The Bureau of Mines Research and Development Laboratory of the Office of Synthetic Liquid Fuels studied the effect of alkali in cemented [iron particles cemented into granules by addition of $Al(NO_3)_3$ or other binding agent], fused, and precipitated iron catalysts. A series of al-

[107] C. C. Hall, S. R. Craxford, D. Gall, and S. L. Smith, PB 91,925 (1948), 7 pp; *B.I.O.S. Final Rept.* 1,712, Item 30.

[108] F.I.A.T. Reel 116-X, Frames 1,631–72, 13th Communication, 1,693–6.

kalized cemented catalysts was prepared from finely divided magnetite ore which had been concentrated by magnetic separation. The procedure for preparing the catalysts was as follows: The finely divided magnetite ore was mixed in a large evaporating dish with a 30 per cent solution of $Al(NO_3)\cdot 9H_2O$ in the proportions equivalent to $100Fe: 3.5Al_2O_3$. The mixture was evaporated to dryness while it was constantly stirred and was then dried in an electric oven at 150°C for about 15 hr. The product was broken up and the 6–8 mesh granules collected and heated at 500°C for 16 hr. Analysis of a sample of the catalyst at this point showed that its composition was as follows, in per cent by weight: 69.3 total Fe, 14.8 Fe^{+2}, 54.3 Fe^{+3}, 2.06 Al_2O_3, 0.04 K_2O, and 0.04 Na_2O. Portions of the catalyst were alkalized with varying amounts of K_2CO_3 by making a paste of the catalyst and the alkali solution and evaporating the mixture to dryness. Final drying was done for 15 hr at 150°C.

In the synthesis tests, the catalyst samples were reduced for 20 hr at 450°C in dry hydrogen flowing at 1,000 cc per g of catalyst per hr and were tested at 7 atm of $1H_2 + 1CO$ gas, an hourly space velocity of 100,

TABLE 55. INFLUENCE OF ALKALI CONTENT OF CEMENTED IRON CATALYSTS ON ACTIVITY AND PRODUCT DISTRIBUTION IN TESTS AT 7 ATM OF $1H_2 + 1CO$ GAS AND HOURLY SPACE VELOCITY OF 100 (U. S. BUREAU OF MINES)

K_2O, per cent of Fe	0.07	0.16	0.54	0.59	1.35	2.36
Test, X . . .	167	179	196	153	191	186
Catalyst number	A3218.00	A3218.01	A3218.087	A3218.05	A3218.125	A3218.20
Time, weeks	3	5	8	7	2	1
Average temperature, °C	280	256	228	232	262	264
Total acid number of aqueous + hydrocarbon phases	1.58	1.35	4.78	4.76	16.15	23.09
Product distribution, weight per cent						
CH_4	20.1	16.9	8.0	6.6	17.3	18.7
C_2	11.0	8.6	4.9	5.4	10.0	8.8
$C_3 + C_4$	25.4	19.2	10.4	12.4	14.5	12.4
C_1–C_4	56.5	44.7	23.3	24.4	41.8	39.9
C_5+						
<185°C	22.4	24.5	18.0	18.6	17.9	27.7
185°–352°C	17.5	24.8	26.1	22.8	19.8	25.3
352°–464°C	2.4	5.9	11.4	10.3	8.5	6.4
>464°C	0.6	1.6	21.2	23.9	11.9	0.8
Infrared analysis of distillation cuts, weight per cent						
185°C, OH	0.23	0.60	3.64	4.34	2.54	2.41
α-Olefin	1.62	1.15	6.70	5.86	8.60	7.98
Other olefins	8.40	7.08	1.09	1.56	0.14	0.14
185-352°C, OH	0.02	0.02	0.67	0.70	0.36	0.49
α-Olefins	0.20	0.17	2.05	2.29	2.44	5.24
Other olefins	3.59	3.39	2.26	2.34	0.47	0.32

and a temperature varied to maintain a gas contraction (CO_2-free) of 63–65 per cent. The test data, presented in order of increasing K_2O content, are summarized in Table 55.[109] The tests showed that alkali was necessary for a good catalyst and that the optimum K_2O content, with respect to the life of the catalyst, was about 0.6 part per 100 parts of Fe. The two catalysts that contained this quantity of alkali were operated at low temperatures of about 230°C and showed no disintegration upon removal from the reactor, as indicated in Table 56. This information is

Table 56. Condition of Catalyst at Termination of Test

K_2O Content, per cent of Fe	Condition on Removal
0.07	85 per cent dropped freely; top 15 per cent remained in reactor and contained wax and carbon.
0.16	Dropped freely; very little disintegration.
0.54	Dropped freely; no disintegration.
0.59	Dropped freely; no disintegration.
1.35	Reactor plugged; catalyst contained wax and carbon; considerable disintegration.
2.36	Reactor plugged; complete disintegration.

interpreted on the assumptions that the formation of an iron carbide in the catalyst is essential to high activity and that the presence of alkali increases the rate of carbide as well as free-carbon formation. These assumptions are in agreement with the experimental work of Pichler and Merkel.[110] Thus, in catalysts containing small amounts of alkali, the carbide phase was formed slowly and its formation was accompanied by increasing activity, *ie*, lower temperatures of operation. In test X167, the initial temperature was 290°C and it decreased to 275°C; this high initial temperature caused sufficient deposition of free carbon to result in plugging of part of the catalyst. At 0.6 per cent of K_2O, carbide formation was sufficiently rapid so that the operating temperature remained constant and free carbon was not formed in large amounts. In catalysts containing more than 1 per cent of K_2O, the rate of carbide and free-carbon deposition was very rapid; rapid decrease in activity was probably the result of disintegration of the catalyst structure. These catalysts showed loss in granular structure and were present in the form of a heavy paste, which smelled strongly of organic acids when removed from the reactor. The total carbon content increased with alkali content, as shown in Figure 38, in which the total carbon deposited per week is plotted against alkali content. The subject of free-carbon and carbide

[109] B. Seligman, J. F. Shultz, and R. B. Anderson, *Ind. Eng. Chem.*, to be published.
[110] H. Pichler and H. Merkel, *U. S. Bur. Mines Tech. Paper* 718 (1949), 108 pp.

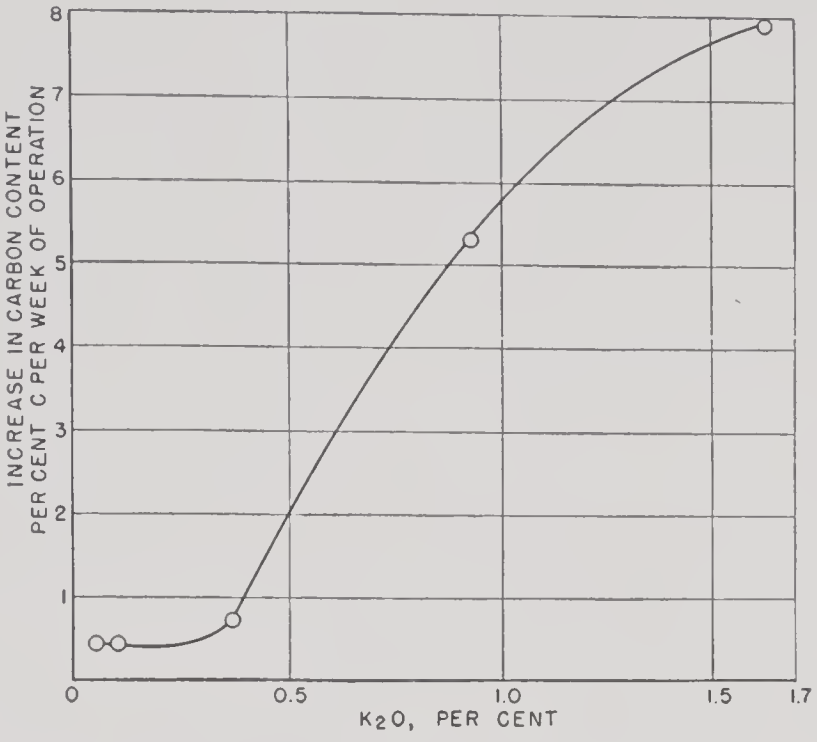


FIGURE 3–38. Effect of alkali on the rate of formation of carbon on the catalyst. Unpublished work of U. S. Bureau of Mines.

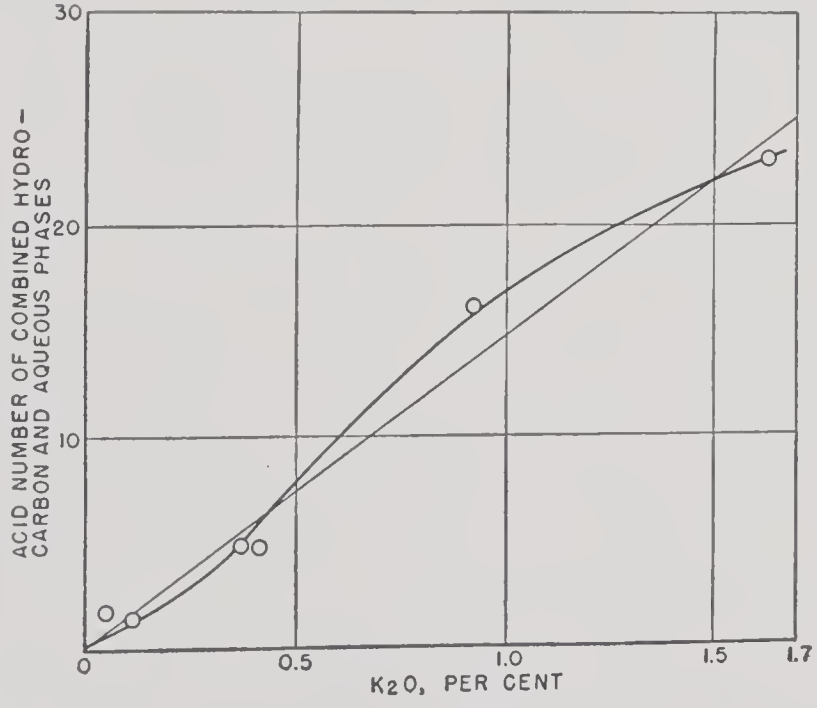


FIGURE 3–39. Effect of alkali on acid production in iron catalyst. Unpublished work of U. S. Bureau of Mines.

formation is discussed at length in Chapter 6, p 464. In Figure 39, a plot of acid number of the combined aqueous and hydrocarbon phases versus alkali content of the catalyst shows the same trend. Variation in operating temperature also affected the formation of acids, which decreased with increasing temperature.

The product distribution was difficult to correlate with alkali content in these tests because of the sharp variation in synthesis temperatures. The average molecular weight and alcohol concentration were at a maximum in the tests operated at low temperatures. The ratio of α-olefins to β- and other olefins increased with alkali content. Thus, if α-olefins are the primary product, the presence of alkali decreases the rate of their isomerization.

When the binding agent was 5 per cent of borax ($Na_2B_4O_7$), an active catalyst was produced. However, a catalyst containing potassium borate ($K_2B_4O_7$) and one containing borax to which 0.5 per cent of K_2O had been added were not active. These observations suggest that K_2O in the presence of B_2O_3 is a poison to this type of catalyst.

Precipitated and fused iron catalysts showed a similar effect of the influence of alkali, as indicated by the data summarized in Table 57.[109]

Table 57. Influence of Alkali Content of Precipitated and Fused Iron Catalysts upon Activity and Products in Tests at 7 Atm of $1H_2 + 1CO$ Gas (U. S. Bureau of Mines)

	Precipitated			Fused	
Catalyst	P3003.040	P3003.042	P3003.043	P2007	A3207 [a]
K_2O, per cent of Fe	0 [b]	0.34 [b]	0.68 [b]	0 [b]	0.40 [c]
Test, X . . .	130	224	211	222	210
Time, weeks	7	5	6	4	6
Space velocity	109	112	100	91	98
Average temperature, °C	265	261	254	268	254
Contraction, per cent [d]	66.7	66.7	65.3	65.0	62.7
Production distribution, weight per cent					
CH_4	20.5	15.3	11.2	18.7	13.8
C_2	14.3	15.7	11.3	10.3	7.5
$C_3 + C_4$	24.1	27.2	22.6	25.4	18.8
C_1–C_4	65.0	58.2	42.7	55.4	43.1
C_5+	35.0	41.8	57.3	44.6	56.9

[a] P2007 + K_2CO_3.
[b] Estimated from starting materials.
[c] Calculated from analysis.
[d] CO_2-free.

The precipitated catalysts were prepared by adding to a solution of the metal nitrates containing iron and copper in the ratio of 100:10 a solution of sodium carbonate. Eighty per cent of the precipitant was added at room temperature, after which the mixture was heated to 70°C and the remaining (5 per cent excess) boiling carbonate solution was added. The slurry was heated to 100°C, boiled for about 1 min, and filtered.

The filter cake was washed with hot distilled water until the wash water was nitrate-free. The catalyst was alkalized by making a paste of the wet filter cake with a solution of the calculated amount of K_2CO_3 and evaporating the mixture to dryness. Final drying was done for 15 hr at 100°–110°C. In preparation of the fused catalysts tested in Table 57, finely divided magnetite ore was mixed with powdered Al_2O_3 in the ratio of $100Fe:4.5Al_2O_3$ and the mixture fused in an iron pot lined with magnetite by an electric current between two water-cooled iron electrodes. After the fused melt had cooled, it was broken into 6–8 mesh granules. The catalyst was alkalized by impregnation with KNO_3 by the same procedure described for alkalization of the cemented catalysts.

The effect of alkali content on usage ratio of $H_2:CO$ is shown in Table 58.[109] Data obtained from tests of a fused synthetic-ammonia-type

Table 58. Effect of Alkali Content of Iron Catalysts on $H_2:CO$ Use Ratio in Tests at 7 Atm of $1H_2 + 1CO$ (U. S. Bureau of Mines)

Test, X . . .	K_2O, per cent of Fe	Synthesis Temperature, °C	Use Ratio of $H_2:CO$
	Cemented catalysts (A3218 series)		
167	0.07	280	0.81
179	0.16	256	0.71
196	0.54	228	0.75
153	0.59	232	0.70
191	1.35	262	0.79 [a]
186	2.36	264	0.78 [a]
	Precipitated catalysts (P3003 series)		
130	0	265	0.89
224	0.34	261	0.68
211	0.68	254	0.64
	Fused catalysts (P2007 and A3207)		
222	0	268	0.83
210	0.40	254	0.71

[a] These values are uncertain; based upon data from only 1 week of operation.

catalyst of various particle sizes indicated that the use ratio was independent of operating temperature, as shown below:

Test, X . . .	Synthesis Temperature, °C	Use Ratio of $H_2:CO$
212	266	0.76
152	256	0.72
118	238	0.77
201	220	0.78

Thus, it was unlikely that variations in the temperature of the tests in Table 58 influenced the use ratio of H_2:CO. The data in this table may then be interpreted to indicate a slight decrease in use ratio with increase in alkali content. This conclusion is in agreement with data obtained by Ruhrchemie in laboratory tests with an alkalized, precipitated iron catalyst of which the composition was 100Fe:5Cu:10CaO:30 kieselguhr.

TABLE 59. EFFECT OF ALKALI IN PRECIPITATED IRON CATALYST, 100Fe:5Cu:10CaO:30 KIESELGUHR, FOR SYNTHESIS AT 220°C AND 10 ATM OF $1H_2 + 1CO$ GAS, WITH RECYCLE OF RESIDUAL:FEED GAS = 2.2:1 (RUHRCHEMIE)

Test	Alkali		Reduction Value, per cent [a]	Synthesis Conditions				
	Potassium Compound	K_2O Content, per cent of Fe		Temperature, °C	U [b]	M_v [c]	X [d]	Average X [d]
714	Water glass [e]	0.5	..	210	40	20	1.0	1.0
715	Water glass	0.5	62	215	70	22	1.2	
726	Water glass	0.5	..	214	58	22	0.9	
712	Water glass	0.5	71	223	45	20	1.0	
721	Water glass	1.1	62	220	59	19	0.79	0.81
723	Water glass	1.1	67	211	37	12	0.75	
717	Water glass	1.1	..	215	52	20	0.9	
709	Carbonate	2.0	75	220	60	20	0.75	0.73
700	Hydroxide	2.5	63	223	55	11	0.72	

[a] Acetic acid method.
[b] Per cent $CO + H_2$ converted.
[c] CH_4, per cent of $CO + H_2$ converted.
[d] Use ratio, H_2:CO.
[e] Composition: 342SiO_2, 111K, and 21Na, g per l.

This catalyst was precipitated by adding a boiling solution of the metal nitrates to a boiling solution of sodium carbonate (for further details see p 263, this chapter); the kieselguhr was mixed into the slurry. After filtration, the filter cake was impregnated with KOH, K_2CO_3, or potassium water glass containing, in grams per liter, 342 SiO_2, 111 K, and 21 Na. The catalyst in the form of 3-mm granules was reduced with $75H_2$-$25N_2$ at about 300°C and an hourly space velocity of 5,000–6,000 for 1 hr. The data summarized in Table 59 [m] were obtained in tests of

[m] T.O.M. Reel 42, Bag 3,439, Item 22, Frames 343–414.

200–1,000-hr duration at 10 atm of $1H_2 + 1CO$ gas, with recycle of residual:feed gas of 2.2:1. The decrease in use ratio with increase in alkali content is evident. Also, a decrease in methane production was indicated, which may be interpreted to mean that a corresponding increase in the higher-molecular-weight fractions occurred.

DECOMPOSITION AND PRECIPITATED CATALYSTS

The first catalysts of Fischer were prepared by decomposition of the metal nitrates and were obtained as fine powders of the metal oxides or were deposited upon carriers. This procedure was recommended by Fischer [5] for the preparation of the alkalized iron-copper (4:1) catalyst, for example. Alkali was introduced in either of two ways: by depositing the iron-copper oxides on Stüttgart carrier, which consisted of sand particles mixed with a few per cent of sodium water glass as binder, or by adding potassium carbonate to the iron-copper oxides mixture. The procedure was as follows: A steel-lined revolving drum was charged with 4–6-mm granules of Stüttgart carrier, and then with crystalline ferric and copper nitrates. The mixture was heated to 130°C in 25–30 min and kept at that temperature for about 30 min. Then the temperature was raised to 220°C in 35 min. The mixture was then allowed to cool gradually. It was reported that heating for too long or at too high a temperature produced a poor catalyst, possibly as a result of interaction of silicic acid in the carrier with the metal oxides. The powdered catalyst was similarly prepared by decomposing the nitrates and then adding potassium carbonate dry or in aqueous solution. The catalyst was reduced in the converter at synthesis temperature with the synthesis gas, which was usually water gas. These catalysts were not satisfactory under the conditions of synthesis then in use. Later, moderately active decomposition catalysts were obtained. Pichler [32] reported that experiments conducted at the Kaiser Wilhelm Institut für Kohlenforschung (KWI) with catalysts of this type at 15 atm of $3CO + 2H_2$ and 240°C gave satisfactory conversion after pretreatment of the catalyst with the same gas at atmospheric pressure and 250°C. By increasing the temperature 2°–3°C each week, conversion could be kept constant for more than 6 months.[112]

The successful precipitation of nickel and cobalt catalysts in 1931–1932 led to the study of iron catalysts prepared by the same technique. These iron catalysts were found to be active at 235°–255°C, especially after methods of pretreatment and operation (at medium pressures of about 10–15 atm) had been developed. In the Ruhrchemie laboratory

[112] German Patent Applic. St 56,856, Nov. 23, 1937.

in which kieselguhrs and kieselguhr-containing cobalt catalysts were intensively studied, iron catalysts were precipitated on kieselguhr. Indeed, the Ruhrchemie considered the absence of kieselguhr in the KWI iron catalysts an important disadvantage in large-scale manufacture, particularly during filtration. Other carriers, such as water glass, Luxmasse, and dolomite, were also used by the other German companies that were developing iron catalysts. In 1943–1944, the KWI, Ruhrchemie, and Rheinpreussen did development work on highly active precipitated catalysts which could be successfully operated at synthesis temperatures of about 220°C and low pressures (10 atm to atmospheric).

Promoters

Effect of copper. The effect of varying the amount of copper incorporated in the decomposition catalyst of Fischer is shown by the results in Table 60.[5] The catalysts containing iron and copper in the ratios

Table 60. Effect of Copper Concentration upon Activity and Yields of Fe-Cu Catalyst

(Fe and Cu oxides on Stüttgart carrier, 70 g of catalyst, 30-cm layer of catalyst tested with water gas at 250°C and flow of 4 l per hr.)

Fe:Cu Ratio	Time, hr	Contraction, per cent	Hydrocarbons, g per cu m $1H_2 + 1CO$			CO_2 in Product Gas, per cent	Contraction	
			CH_4	C_1–C_4	C_5+		Hr	Per Cent
9:1	41	25	8.5	42.0	19.9	20.1	64	6
4:1	28	35	13.0	58.2	38.1	33.2	117	14
2:1	24	37	15.0	60.8	34.7	31.2	112	27
1:1	41	33	14.9	55.6	17.2	32.3	116	26

of 4:1 and 2:1 produced the highest yields of liquid hydrocarbons. The yield of hydrocarbons boiling in the gasoline range was slightly higher from the 4Fe:1Cu catalyst. In all four experiments, which were done at atmospheric pressure of water gas, carbon dioxide was the chief secondary product. The iron-rich catalyst (9Fe:1Cu) was less durable than the others; the contraction in this test dropped to 6 per cent in 64 hr. It is of interest to observe that Fujimura [113] could find little, if

[113] K. Fujimura, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **29**, 280–4 (1936).

any, difference in catalytic activity during atmospheric-pressure synthesis with iron-copper catalysts containing iron and copper in the ratios 1:2, 1:1, 3:1, and 5:1.

The presence of large quantities of copper (20–25 per cent, based on iron) had a deleterious effect upon the life of iron catalysts at high temperatures, probably because of the alloying of iron with copper or sintering of the catalyst particles. High temperatures, *ie*, over 250°C, were reached during synthesis at atmospheric pressure and in the early tests in the medium-pressure synthesis. Later, temperatures of more than 300°C were used in certain pretreatment techniques (at KWI) for the preparation of catalysts for medium-pressure synthesis. As a consequence, the iron catalysts developed for medium-pressure synthesis usually contained less than 10 per cent of copper, by weight of iron.

Other promoters. In addition to alkali and copper, other materials have been reported to promote the activity of Fischer-Tropsch iron catalysts. Tsuneoka and his coworkers [114–117] and Kita [118] incorporated the following promoters in iron-copper-kieselguhr catalysts: K, Mn, Rb, H_3BO_3, Ni, and Co. Two catalysts, of composition 4Fe:1Cu:5 kieselguhr:0.08K_2CO_3 and 4Fe:1Cu:5 kieselguhr:0.08K_2CO_3:0.08Mn, were prepared by Tsuneoka by mixing solutions of the nitrates with unpurified kieselguhr and precipitating with a solution of an equivalent amount of alkali carbonate. The precipitate, after filtration and washing, was impregnated with a small amount of potassium carbonate, air dried at 100°C, and pulverized. The yields were 83 and 88 cc of liquid hydrocarbons, respectively, per cu m of a gas containing equal parts of hydrogen and carbon monoxide, when 3.8 l per hr per 4 g of iron was employed at 250°C. A catalyst of which the composition was 4Fe:1Cu:5 kieselguhr:0.08Rb_2CO_3:0.08Mn resulted in a yield of 90 cc per cu m. When 3 per cent Al_2O_3 was added to the iron-copper-kieselguhr-potassium carbonate-manganese catalyst after precipitation, the hydrocarbon yield was increased to 94 cc per cu m. The oxygen appeared

[114] S. Makino, H. Koide, and Y. Murata, *ibid.*, **37,** 350–65 (1940); *J. Soc. Chem. Ind. Japan,* **43,** Suppl. Binding, 235–41 (1940).

[115] Y. Murata and S. Makino, *Sci. Papers Inst. Phys. Chem. Research (Tokyo),* **37,** 338–49 (1940); *J. Soc. Chem. Ind. Japan,* **43,** Suppl. Binding, 210–5 (1940).

[116] Y. Murata, S. Makino, and S. Tsuneoka, *Sci. Papers Inst. Phys. Chem. Research (Tokyo),* **35,** 348–55, 356–64 (1939); *J. Soc. Chem. Ind. Japan,* **42,** Suppl. Binding, 114–21 (1939).

[117] S. Tsuneoka, Y. Murata, and S. Makino, *Sci. Papers Inst. Phys. Chem. Research (Tokyo),* **35,** 330–6, 337–47 (1939); *J. Soc. Chem. Ind. Japan,* **42,** Suppl. Binding, 107–14 (1939).

[118] G. Kita, U. S. APC SN272,175, May 6, 1939, U. S. APC SN391,721, May 4, 1941; British Patent 529,390, Nov. 20, 1940.

entirely as carbon dioxide rather than as water, which is the main oxygen-containing product of cobalt and nickel catalysts. Kita's catalyst contained iron, copper, kieselguhr, manganese, and boric acid in the ratio 4:1:5:0.08:0.08 and an indeterminate quantity of alkali as potassium carbonate and hydroxide. The optimum amounts of copper and K_2CO_3 for this catalyst were found to be 20–40 per cent and 2–3 per cent, respectively. The addition of 5 per cent of nickel or cobalt enhanced the activity for $2H_2 + 1CO$ synthesis gas but was undesirable for gas containing $1H_2 + 1CO$. Formation of water was observed when the catalyst contained more than 2.5 per cent of nickel. The addition of thoria or urania to an iron catalyst containing 10 per cent of nickel did not appreciably affect its activity.

Calcium oxide and copper were the chief promoters used by Ruhrchemie. When interrogated in 1945, Roelen stated that several thousand trial batches of iron catalysts had been prepared in the Ruhrchemie laboratories and that catalyst tests had been made on a scale varying from 50 cc to 1,000 l of catalyst. Although it was known that variations in the calcium oxide and copper content of the catalyst affected the activity, particularly the use ratio of H_2:CO, research had been temporarily restricted to catalysts with a fixed ratio 100Fe:5Cu:10CaO, so that the influence of other variables could be investigated. Roelen [35] thought that there was little difference in catalytic effect between aluminum oxide as used by Lurgi and calcium oxide as used by Ruhrchemie.

Rheinpreussen described a catalyst for normal-pressure synthesis in which magnesium was a promoter; its composition was 100Fe:10Cu:20Mg:50 kieselguhr:$1K_2CO_3$.[108] Into the solution of metal nitrates, containing 50 g Fe per l, was stirred the kieselguhr. The slurry was added to a 20 per cent solution of sodium carbonate containing 10 per cent more precipitant than the stoichiometric equivalent. The mixture was heated to boiling, filtered, and washed several times with a sevenfold quantity of hot distilled water, calculated on the iron content. The wet filter cake was alkalized by impregnation with aqueous K_2CO_3 and dried at 110°C. The iron density, or content, of the dry catalyst was 200 g Fe per l. Magnesium was incorporated into other Rheinpreussen catalysts, described later in this chapter (p 268), through the use of the carrier, dolomite, in which magnesium is one of the chief constituents.

Beginning early in 1940, research on iron catalysts to replace cobalt for the production of wax suitable for oxidation was undertaken in the I.G. Farben. Ammonia Laboratory at Oppau.[70] The first catalyst that showed promise had the composition, 100Fe:25Cu:$100Al_2O_3$:10K (Table 61, column 1), and was prepared by dropwise precipitation over a

TABLE 61. DEVELOPMENT OF PRECIPITATED 100Fe:25Cu:50MgO:(6–8)K:50 KIESELGUHR WAX-PRODUCING CATALYST FOR MEDIUM-PRESSURE SYNTHESIS (OPPAU)

(Single-stage operation at 12 atm of $1CO + 2H_2$ gas and space velocity of 240.)

	1	2	3	4	5	6	7	8	9	10
Catalysts,[a] $MgO(Al_2O_3)$-K-SiO_2	(100):10:0	MgO:K:SiO_2 [b]	36:6:50	48:6:48	42:11:49	47:12:95	34:10:88	32:7:91	89:8:49	95:8:48
Synthesis temperature, °C	210	235	210	210	222	210	225	215	218	230
CO converted, per cent	80	70	53	46	71	50	52	56	63	66
Yield										
C_5+, g per cu m $1CO + 2H_2$ gas	82	90	86	67	88	72	78	75	91	99
CH_4, g per cu m $1CO + 2H_2$ gas	..	..	14	12	21	14	..	..	14	12
Distribution, C_5+, weight per cent										
Gasoline, <195°C	23	40	30	43	48	24	22	46	46	30
Diesel oil, 195°–320°C	18	15								
Soft wax, 320°–450°C	24	20	70	57	52	76	78	54	54	70
Hard wax, >450°C	35	25								
Composition, >320°C fraction										
Straight chains, per cent [c]	91	81	95	85	94	92	88	84	93	86
Olefins, per cent	8	8	23	28	14	6	22	19	13	25
Alcohols, per cent	6	3	5	2	4	2	4	5	3	7

[a] Catalysts all contained 100Fe:25Cu in addition to constituents shown.

[b] Precise composition not given.

[c] Degree of branching determined by empirical method of Schaarschmidt, using antimonypentachloride.

time interval of 2 days. Synthesis with this catalyst in 15-mm-I.D. electrically heated, gas-phase, catalyst-testing reactors at 12 atm of $1CO + 2H_2$ gas and a space velocity of 240 volumes of feed gas per volume of catalyst per hour could be carried out for a maximum of 135 days at a constant temperature of 210°C without any loss in activity. However, during this time the distribution of products shifted, owing to a decrease in paraffin yield from 60 to 45 per cent.

Since the preparation of this catalyst was laborious, the substitution of the promoter, aluminum oxide, by magnesium oxide was investigated. The first problem of mechanical disintegration of magnesium oxide-containing preparations was overcome by using kieselguhr as the carrier. The results shown in Table 61, column 2, indicated that the magnesium oxide-promoted catalyst produced a somewhat higher yield but also operated at a higher temperature and resulted in a larger gasoline fraction than the alumina-promoted catalyst. This drawback was overcome by reduction with hydrogen at a low temperature of 180°–250°C and a high space velocity of 5,000; this procedure permitted lowering of the synthesis temperature by 15°–20°C. Other advantages of the magnesium oxide-containing catalysts were the following: (1) simple and quick preparation, since the difficulties encountered in washing and drying the gel structure of substances like aluminum hydroxide were absent; (2) variations in proportions of the constituents were permissible, as shown in Table 61, columns 3–10, without seriously affecting the synthesis.

The optimum composition of the catalyst was 100Fe:25Cu:50MgO:(6–8)K:50 kieselguhr. It was precipitated by passing the nitrate solution of iron, copper, and magnesium and the solution of potassium carbonate through a blending nozzle at such a rate that the *p*H remained constant. The precipitate was mixed with a kieselguhr slurry or a silica gel containing small pores, heated for 10 min, and then washed by decantation. The washed and dried catalyst was broken into 1–3-mm granules whose bulk density was 0.4 g per l.

Results of four-stage, medium-pressure, gas-phase, pilot-plant tests of three magnesium-promoted catalysts of the type described above are tabulated in Table 62. Reduction of the catalyst took place within the converter with hydrogen passed at a space velocity of 1,000 and a temperature of 220°C, for 24 hr. The four-stage synthesis operation was conducted in four reaction tubes each 5 m in length, 16 mm I.D., and containing a catalyst zone 4.5 mm long of which the capacity was 0.8–1.0 l of unreduced catalyst. The test data show that more than half of the C_5+ product was wax boiling above 320°C; more than 75 per cent of this fraction consisted of saturated straight-chain hydrocarbons.

TABLE 62. PILOT-PLANT TESTS OF PRECIPITATED IRON, MAGNESIUM-PROMOTED CATALYSTS (I.G. FARBEN. AMMONIA LABORATORY, OPPAU)

Time, days	121	141	42
Test number	587/590	620/623	677/680
Catalyst number	1,382	1,383	1,462
Catalyst analysis, per cent			
Fe	23.6	24.2	23.4
Cu	5.6	6.2	6.2
MgO	2.1	7.4	8.3
SiO_2	33.7	23.3	22.2
K	2.4	2.5	3.0
CO_2	2.2	6.0	6.0
Synthesis gas, ratio $CO:H_2$		0.9–1:1 [a]	
Utilization ratio, $CO:H_2$		1.1–1.2:1	
Hourly space velocity, l gas per l catalyst per hr		120	
Synthesis temperature, °C	240	230	225
Yield of primary product + gasol, g per cu m $1CO + 1H_2$	147	145	142
Space-time-yield, kg product per l per catalyst per day	0.42	0.42	0.41
Contraction, per cent	53	57	51
CO conversion, per cent	83	83	70
Per cent CO converted to			
CO_2	33	32	25
CH_4	3	4	2
Higher hydrocarbons	47	47	43
Total	83	83	70
Distribution, weight per cent			
Gasoline, <195°C	19	24	21
Middle oil, 195°–320°C	15	23	18
Paraffin, >320°C	66	53	61
	100	100	100
Composition of middle oil (195°–250°C), per cent			
Olefins	63	53	48
Alcohols	18	16	13
Straight chains	48	42	52
Composition of middle oil (250°–320°C), per cent			
Olefins	52	42	47
Alcohols	16	14	12
Straight chains	64	68	70
Composition of paraffin (320°–450°C), per cent			
Olefins	35	28	34
Alcohols	8	9	10
Straight chains	80	77	83

[a] Sulfur-free; contained 2 per cent N_2 and no CO_2.

Source of Iron

At the Kaiser Wilhelm Institut für Kohlenforschung (KWI), it was found that preparations obtained from ferrous (Fe^{+2}) salts were not satisfactory catalysts.[101] For example, a ferrous iron catalyst was prepared by dissolving iron shavings in several portions in nitric acid of maximum initial density of 1.05, at a temperature between 35°–40°C. Preneutralization of the iron solution, which contained 1 kg Fe per 30 l of solution, with sodium carbonate was done in the cold. Then the mixture was heated to 70°–75°C and precipitated by sodium carbonate solution. Subsequent heating of the precipitate, filtration, washing, alkalization, and drying were done in the manner described for the "normal" iron catalyst (this chapter, p 248). The dry, ferrous iron catalyst cake was voluminous and earth-brown in color; it showed none of the gel-like properties of the normal catalyst. After pretreatment at 325°C and 0.1 atm of CO, this catalyst became deactivated in the first few days of synthesis at 235°C and 15 atm of $3CO + 2H_2$ gas (Table 63, column 2). The same results were observed with catalysts prepared from ferrous chloride, as shown in columns 3 and 4 of Table 63.

Table 63. Ferrous (Fe^{+2}) Iron Catalysts in the Medium-Pressure Synthesis (KWI)

(15 atm of $3CO + 2H_2$, throughput 4 l per 10 g Fe per hr.)

1 Catalyst[a]	2 *x* $Fe(NO_3)_2$		3 *x* $FeCl_2$		4 *x* $FeCl_2$		5 Fe^{+2}-Cu(5:1)	
Time, days	Temperature, °C	Contraction, per cent	Temperature, °C	Contraction, per cent	Temperature, °C	Contraction, per cent	Temperature, °C	Contraction, per cent
1	235	56	235	57	235	56	...	..
2	235	57	235	57	225	56	...	..
3	235	40	235	34	225	49	...	..
4	...	.	235	30	215	38	...	..
5	...	.	...	..	225	35	...	..
6	...		...	..	225	29	...	..
10	...	..	...	..	..	..	257	42
20	...	..	...	..	...	..	265	50
30	...	..	...	..	..	..	270	53
40	..	..	...	..	...	..	274	53
50	..	..	...	..	...	..	275	55
60	..	..	...	..	...	..	272	52
90	...	..	...	..	...	..	281	51
120	..	.	...	..	...	..	285	49
150	...	.	...	..	..	..	290	47

[a] All catalysts except that in column 5 were inducted at 325°C and 0.1 atm of CO. Catalyst in column 5 was inducted at 245°C, $1CO + 2H_2$ at atmospheric pressure, 4 days, throughput 4 l per 10 g Fe per hr.

A ferrous iron-copper (5:1) catalyst, pretreated at 245°C with $1CO + 2H_2$ gas at atmospheric pressure for 4 days, was somewhat more active in synthesis at 15 atm of $3CO + 2H_2$ gas (Table 63, column 5). However, high synthesis temperatures were necessary to maintain the contraction above 50 per cent. This contraction included the CO_2 and was equivalent to 70 per cent conversion. The Fe^{+2}-Cu catalyst was prepared [101] as follows: 180 g $FeCl_2 \cdot 4H_2O$ (50 g Fe) and 26 g $CuCl_2 \cdot 2H_2O$ (10 g Cu) dissolved in 1 l of water were heated to boiling and precipitated in 0.5–1 min with a solution containing 160 g Na_2CO_3 dissolved in 1.5 l of water. The precipitate was filtered and washed 6 times with 1-l portions of hot water. The filter cake was impregnated with 0.125 per cent of K_2CO_3, based on weight of iron, dissolved in 100 cc of water, and the mixture was then slowly heated on a sand bath. Finally, it was dried at 105°C.

The "normal" or "standard" KWI iron catalyst developed in 1937–1940 for synthesis under the above conditions (235°C and 15 atm of $3CO + 2H_2$ gas) consisted chiefly of ferric iron and was prepared under such conditions that some ferrous iron was present. It contained either no copper or a very small quantity of about 1 per cent, which was enough to make the preparation of the catalyst reproducible and to facilitate reduction and carburization of the iron in the catalyst. It contained also 0.25 per cent of K_2CO_3, based on weight of iron, which increased the higher-molecular-weight fractions of the product. The normal catalyst was prepared [37] by dissolving iron in nitric acid under fixed conditions. Technical iron filings were introduced in small portions into nitric acid of an initial density of 1.18 at a temperature below 40°–50°C. The iron solution containing 1 kg of iron per 30 l of solution was preneutralized in the cold with sufficient sodium carbonate solution (1 kg per 8–10 l H_2O) to preclude the formation of a permanent precipitate. The mixture was heated to boiling and precipitated by sodium carbonate solution in slight excess of the stoichiometric equivalent. After precipitation, the mixture was brought to a boil for a minute or two, filtered, and washed free from alkali with hot distilled water. The moist precipitate was repulped in distilled water and made into a uniform slurry on the water bath. Under constant stirring, a solution of 0.25 per cent of K_2CO_3, based on weight of iron, was added. Most of the water was evaporated off on a water bath. Then the catalyst was dried in hot air at 105°–110°C for about 15 hr. The dried cake, which was dark brown, hard, and glassy when broken, was sometimes pelleted (with 5–25 per cent of synthetic paraffin added as die lubricant) and sometimes crushed into 1–3-mm granules.

Table 64 shows the advantage of precipitating at 100°C and boiling

the mixture for a minute. The desirability of some aging of the precipitate is also shown by results of the U. S. Bureau of Mines tests. The standard procedure developed in 1943–1944 for the preparation of active ferric iron catalysts consisted of adding a 4 molar solution of cold anhydrous potassium carbonate to a hot solution containing about 1 mole of ferric nitrate at 70°–90°C over a time interval of 20–30 min.

TABLE 64. INFLUENCE OF PRECIPITATION CONDITIONS UPON ACTIVITY OF IRON CATALYSTS (KWI)

(Catalyst inducted with 4 l CO per 10 g Fe per hr at 0.1 atm and 325°C for 25 hr.)

Precipitation Conditions		Alkali Content, per cent	Per Cent Contraction Obtained in Synthesis Tests [a]				
			Days				
Temperature, °C	Time of Boiling after Precipitation, min		1	2	5	10	20
20	None	1	43	..	44	43	..
60	None	1	50	..	33	20	..
20	<1	1	50	..	48	51	..
20	<1	0.25	..	50	48	51	50
20	1	0.25	55	55	48	48	50
20	5	0.25	..	56	..	47	48
100	1	0.25	50	50	50	49	56

[a] Synthesis conditions: 15 atm of $3CO + 2H_2$, 235°C, space velocity 4 l per 10 g Fe per hr. Highest possible contraction, assuming conversion to proceed according to equation, $2CO + H_2 = CO_2 + CH_2$, was 60 per cent. In actual practice best yields were obtained at a contraction of 50–55 per cent, including CO_2.

The precipitate was washed by decantation until the wash water gave a negative nitrate test with diphenylamine-sulfuric acid reagent. The catalyst cake was permitted to dry at room temperature for about 100 hr and then at 150°C for 20 additional hr. The dried catalyst was gel-like in appearance, hard, very dark brown, and lustrous when broken. It was crushed to pass through a 60-mesh screen; the powder was mixed with powdered graphite and then compressed into hard, well-formed dark-brown pellets (3.2 mm in diameter by 2.4 mm in length) whose bulk density at maximum packing was 1.3 g per cc. When crushed into 8–14 mesh granules, the bulk density was about 1.

The data obtained from a pelleted catalyst prepared as described above are shown in Table 65, column 2.[119] The catalyst was reduced in the synthesis reactor by hydrogen at an hourly space velocity of 20, while the temperature was gradually raised to 360°C during a period of 20 hr and held at that point for 4 hr longer. The temperature was lowered;

Table 65. Influence of Conditions of Preparation of Pelleted Precipitated Iron Catalysts (U. S. Bureau of Mines Tests with $1H_2 + 1CO$ Gas)

1	2	3	4	5
Catalyst number	10A + 10B part A	10B part C	10B part B	10F part C
$(Fe^{+2}$-$Fe^{+3})$-Cu-K_2CO_3	(0:100):0:0	(0:100):0:0	(0:100):0:0	(0:100):0:0
Source of iron	NO_3^-	NO_3^-	NO_3^-	NO_3^-
Time, hr	1,650	117	93	249
Pressure, atm [a]	7	0	0	7
Space velocity [b]	185	160	160	160
Temperature, °C	246	241	242	245
Contraction, per cent	50	16	34	42
Average C_5+, g per cu m [c]	55.1	10.5	16.7	26.9
Maximum C_5+, g per cu m [c]	76.0	21.0	16.7	52.6
C_5+, weight per cent of total hydrocarbons	68.5	70.0	68.0	57.4
C_1–C_4, g per cu m [c]	25.3	4.5	7.9	20.0

[a] Gauge pressure.
[b] Per hour.
[c] Per cubic meter of feed gas.

water gas was introduced at 7 atm (gauge pressure) and a temperature at which the contraction was not higher than 30 per cent. During the next 36 hr, the temperature was gradually increased to produce a conversion of 50–60 per cent. During the 1,650-hr test at 7 atm of water gas ($1H_2 + 1CO$) and a rather high average temperature of 246°C, the average yield of C_5+ hydrocarbons, per cubic meter of feed gas, was 55.1 g and the maximum yield, 76.0 g.

Too rapid precipitation and too rapid drying of the precipitate produced less active catalysts, as shown by the data in columns 3, 4, and 5 of Table 65 for catalyst 10F part C, 10B part B, and 10B part C, respectively. Catalyst 10F was precipitated very quickly within 2–3 min; 10F part C was dried under the optimum conditions. Catalyst 10B was precipitated properly, but parts B and C were dried very quickly. The advantage gained by slower preparation was probably an aging effect,

[119] H. H. Storch, R. B. Anderson, L. J. E. Hofer, C. O. Hawk, H. C. Anderson, and N. Golumbic, *U. S. Bur. Mines Tech. Paper* 709 (1948), pp 81–4, 91–103, 173–80.

resulting in transition from one form of iron hydroxide to another. It should be noted that the tests in columns 3 and 4 were carried out at atmospheric pressure, which was partly responsible for the low activity of these two catalysts.

Catalysts containing ferric and ferrous iron were developed at the KWI in 1944 and were reported to be highly active catalysts and suitable for use at low synthesis temperatures and pressures. One such catalyst (N50) had the composition $50Fe^{+2}:50Fe^{+3}:1Cu:0.25K_2CO_3$. A more active catalyst of this type was catalyst N75, of which the composition was $75Fe^{+2}:25Fe^{+3}:20Cu:1K_2CO_3$. The following description of its preparation from the chloride salts was reported by Pichler:[32] A solution containing 134 g $FeCl_2 \cdot 4H_2O$ (37.5 g Fe), 61 g $FeCl_3 \cdot 6H_2O$ (12.5 g Fe, total Fe 50 g), and 26 g $CuCl_2 \cdot 2H_2O$ (9.2 g Cu) dissolved in 2 l of water was heated to 70°C. To this solution was added as rapidly as possible a second solution containing 200 g anhydrous Na_2CO_3 dissolved in 2 l of water and heated to boiling. Sufficient sodium carbonate was required to produce a slightly alkaline reaction at the end of the precipitation. The mixture was then heated to 100°C, filtered, and washed free from alkali with several liter-portions of boiling water. The catalyst cake was alkalized in the usual way (see p 248) with potassium carbonate, and then evaporated and dried at 105°C for about 20 hr. No special precautions against oxidation were taken during drying, and, in fact, drying in air was preferable to an inert atmosphere. More ferric salt was required in the original mixture if the catalyst was to be dried in the absence of air. The dried catalyst was broken up and the granules, 2–4 mm in size, were collected by screening.

A sample (80 cc) of this catalyst was pretreated in a water-cooled 10-mm-I.D. reactor with $1CO + 2H_2$ gas at atmospheric pressure, flow rate of 40 l per hr (hourly space velocity 500), and a temperature of 225°C.[29,32] The gas was neither dried nor freed from carbon dioxide. At the end of 48 hr, paraffin was extracted from the catalyst by synthetic oil boiling in the range 230°–300°C. Pretreatment was continued for an additional 24–28 hr. After a second extraction, the catalyst was put into synthesis at 220°C and atmospheric pressure of water gas, at a space velocity of 100. If the space velocity were 50, the starting synthesis temperature could be 210°–212°C. For either set of conditions, the conversion of carbon monoxide was 90–95 per cent, and the total yield, including methane, 140–145 g per cu m $1H_2 + 1CO$ gas. The methane yield was 2–4 g for the lower space velocity and 5–6 g for the higher one. The distribution of the products obtained at a space velocity of 50 and temperature of 211°C is shown in Table 66. The products contained 30–40 per cent wax, boiling range >300°C, and they

varied in color from yellow to brown. More oxygenated compounds were formed than in the cobalt synthesis, the amount being the same as in the medium-pressure iron Reichsamtversuch (this chapter, p 305). The high yield could be maintained for 3 months by extracting paraffin from the catalyst every 2 or 3 days and by raising the temperature 5°C over the 3-month period. Methane production increased a little during this period. The use ratio of H_2:CO of the gas was 0.6, so that no second stage was possible.

Table 66. Hydrocarbon-Product Distribution from $75Fe^{+2}:25Fe^{+3}:20Cu:1K_2CO_3$ Catalyst Obtained During Synthesis with Water Gas at Atmospheric Pressure (*A*) and 10 Atm (*B*) (KWI)

	Weight Per Cent	
Fraction	*A*	*B*
CH_4	2.4	3.2
C_2–C_4	10.1	9.0
Oil, <180°C	13.5	10.0
Oil + wax, >180°C	74.0	77.8
Total	100.0	100.0

After 2 weeks of operation at atmospheric pressure under the conditions described above, the catalyst could be successfully operated in the medium-pressure synthesis. First, the pressure was increased to 2 atm and synthesis continued for another 2 weeks at 212°C and a space velocity of water gas of 100. Subsequent increase in pressure to 10 atm permitted synthesis for 3 months at a constant temperature of 200°C. No extraction with solvent was necessary, although much more wax was formed than at atmospheric pressure. The average yield of products whose distribution for the first month is shown in Table 66 was 143–148 g per cu m $1H_2 + 1CO$, including methane. It was possible to regulate conditions so that 37 per cent of the yield was hard paraffin boiling above 450°C, with no intermediate extraction necessary. The use ratio of H_2:CO was 0.7–0.8.

A catalyst of which the composition was $75Fe^{+2}:25Fe^{+3}:20Cu:1.5K_2CO_3$ was reported by Pichler and Merkel [110] to be their best catalyst for atmospheric-pressure synthesis at a temperature of 220°C. The products were probably similar to those obtained from the corresponding catalyst containing 1 per cent K_2CO_3, and the product distribution was probably shifted toward higher-molecular-weight hydrocarbons, because of the higher alkali content.

The fact that the KWI highly active ferrous-ferric iron catalysts were prepared from the chloride salts of iron appeared to contradict Fischer's earlier reports [5] and the U. S. Bureau of Mines observations [119] that

chloride salts produced poorly active iron catalysts. For example, the U. S. Bureau of Mines data summarized in column 1, Table 67, showed that a catalyst prepared from ferric nitrate solution containing ferric chloride produced an average yield of only 42 g per cu m of feed gas containing $1H_2 + 1CO$, in a test at 261°C and 7 atm (gauge pressure). Even lower yields were obtained from catalysts precipitated from ferric chloride alone. These catalysts were different also in appearance from those precipitated from ferric nitrate, and the difference was apparent even during preparation. The precipitates were yellow-brown, rather than red-brown; they were not voluminous; in the dry state, they were less gel-like and they produced pellets whose bulk density was low (1 g per cc).

Subsequently, a catalyst which was prepared from ferrous, ferric, and cupric chlorides, according to the KWI procedure,[32] produced an average yield of 88.3 g of C_5+ hydrocarbons per cu m of feed gas and a maximum yield of 93 g, when tested for 46 days at 7 atm and an average temperature of 229°C. The data for this test are summarized in column 2, Table 67. The approximate composition of the catalyst (L3004) was $75Fe^{+2}:25Fe^{+3}:20Cu:0.2K_2CO_3$. The catalyst, in the form of 6–8 mesh granules, was inducted with water gas for 25 hr at atmospheric pressure and a temperature of 226°C.

In order to determine whether it was the presence of ferrous iron or copper that made this catalyst active despite the fact that chloride salts were used, tests were made with several preparations in which the constituents of L3004 were varied. The results obtained from this study are shown in Table 67, columns 3–7. Catalyst L2001, prepared by dissolving metallic iron in cold nitric acid so as to produce a mixture of ferrous and ferric nitrates and inducted for 25 hr with 1 atm of water gas at 269°C, produced an average yield of 73.8 g of liquid hydrocarbons per cu m of water gas, at an average temperature of 238°C. This catalyst contained 0.2 per cent of K_2CO_3, based on the weight of iron. The yield of gaseous hydrocarbons was high. From L2002, which contained the same amount of K_2CO_3 and was similarly inducted, a lower yield of 54.8 g of liquid hydrocarbons per cu m of water gas was obtained, at an average temperature of 244°C. The source of iron was ferric nitrate; otherwise, this catalyst was similar in composition to L2001. The product distribution for the two catalysts was the same. In catalyst L2003, of composition $100Fe^{+3}:0.5K_2CO_3$, and L3006, of composition $100Fe^{+3}:10Cu:0.2K_2CO_3$, the source of iron was ferric chloride. As shown in Table 67, these preparations, like the earlier ones prepared from ferric chloride solution, were virtually inactive. Catalyst L3008, of composition $100Fe^{+2}:20Cu:0.5K_2CO_3$, was prepared from ferrous chloride.

TABLE 67. TESTS OF IRON CATALYSTS PREPARED FROM CHLORIDE SALTS (U. S. BUREAU OF MINES)

	1	2	3	4	5	6	7
Catalyst	10M	L3004	L2001	L2002	L2003	L3006	L3008 [a]
$(Fe^{+2}$-$Fe^{+3})$-Cu-K_2CO_3	(0:100):0:0	(75:25):20:0.2	(100):0:0.2	(0:100):0:0.2	(0:100):0:0.2	(0:100):10:0.2	(100:0):20:0.5
Source of iron	NO_3^- [b]	Cl^-	NO_3^-	NO_3^-	Cl^-	Cl^-	Cl^-
Time, hr	776	1,117	1,170	638	138	260	250
Pressure, atm (abs)	7.8	7.8	7.8	7.8	7.8	7.8	7.8
Space velocity [c]	90	100	91	103	97	100	77
Temperature, °C	261	229	238	244	263	282	239
Contraction, per cent [d]	63	66	64	63	28	37	53
Average C_5+, g per cu m [e]	42.0	88.3	73.8	54.8	16.0	12.7	75.8
Maximum C_5+, g per cu m [e]	58.6	92.9	103.0	62.8	16.0	25.1	88.8
C_5+, weight per cent of total hydrocarbons	46.0	72.5	58.5	55.2	32.0	25.2	71.6
CH_4, g per cu m [e]	15.8	9.4	13.5	12.0	7.7	8.7	8.7
C_1-C_4, g per cu m [e]	49.4	33.5	52.3	44.6	34.1	37.6	30.1
CO_2, g per cu m [e]	157.5	346.0	337.7	296.2	90.7	124.2	319.0

[a] Catalyst disintegrated.
[b] KCl added before precipitation.
[c] Per hour.
[d] CO_2-free.
[e] Per cubic meter of feed gas.

After induction at 225°C with water gas at atmospheric pressure for 25 hr, this catalyst was moderately active in a 3-week test at 7 atm of water gas, as indicated by the gas contraction. This catalyst disintegrated in the reactor. From these results, it was evident that the presence or absence of ferrous iron was the significant factor that determined whether catalysts precipitated from chloride solutions would be active in the hydrocarbon synthesis. The explanation for this phenomenon was sought in x-ray studies and chemical analyses of these catalysts.

X-ray diffraction data showed that the inactive catalysts prepared from ferric chloride contained a large proportion of β-$Fe_2O_3 \cdot H_2O$ (or β-FeOOH) in the freshly precipitated, unreduced state; all the catalysts prepared from ferric nitrate consisted chiefly of goethite, α-$Fe_2O_3 \cdot H_2O$ (or α-FeOOH), and hematite, α-Fe_2O_3.[120] Catalysts precipitated from ferric + ferrous salts or only ferrous salts contained magnetite, Fe_3O_4. Because none of the iron oxide phases mentioned above is stable at the temperature of the Fischer-Tropsch synthesis on iron catalysts, it was believed that the deactivating effect of precipitation from ferric chloride resulted not from the presence of β-$Fe_2O_3 \cdot H_2O$ but from some characteristic that it imparted to the eventual catalyst.

Data of Kolthoff and Moskowitz [121] indicated that the chloride ion did not simply adsorb on β-$Fe_2O_3 \cdot H_2O$, but instead it exchanged slowly with the OH groups present both on the surface and in the interior of the crystallite, according to the equation,

$$\beta\text{-FeOOH} + Cl^- \rightarrow \beta\text{-FeOCl} + OH^-$$

and became a part of the crystal structure. A more descriptive formula was thus β-FeO[OH,Cl]. This observation explained the difficulty in washing β-$Fe_2O_3 \cdot H_2O$ free of chloride, which was reported by Weiser and Milligan [122] and was also encountered in the U. S. Bureau of Mines catalysts precipitated from ferric chloride. Chemical analysis showed that the chloride content of the latter catalysts was at least 20 times greater than that of the more active catalysts, which contained ferrous iron. The chloride contents for four of the catalysts are shown below:

Catalyst	Cl^-, per cent of sample
L3004	0.04
L3008	0.02
L2003	0.56
L3006	0.92

[120] L. J. E. Hofer, W. C. Peebles, and W. E. Dieter, *J. Am. Chem. Soc.*, **68**, 1,953–6 (1946).

[121] I. M. Kolthoff and B. Moskowitz, *ibid.*, **58**, 777–9 (1936).

[122] H. B. Weiser and W. O. Milligan, *ibid.*, **57**, 238–41 (1935).

The explanation of the deactivating effect of chloride seems, therefore, to be the following: (1) In the presence of chloride and ferric iron alone, β-$Fe_2O_3 \cdot H_2O$ was produced, which retained chloride in the crystal structure. During synthesis, chloride present on active metal deactivated the catalyst. (2) In the presence of chloride and ferrous and ferric iron (at least 35 per cent Fe^{+2}) or chloride and ferrous iron alone, the formation of β-$Fe_2O_3 \cdot H_2O$ was inhibited. Instead, magnetite, Fe_3O_4, or ferrous hydroxide, $Fe(OH)_2$, or a mixture of both was formed; from this crystal structure chloride was easily removed by washing.

Iron catalysts tested at the British Fuel Research Station were precipitated from ferric nitrate and/or ferrous chloride and contained in addition 5–25 parts by weight of copper and 0.1–3 of alkali (K_2O).[123] No iron catalyst consistently produced the good yields obtainable from cobalt catalysts at 10 atm. In the pressure range of 10–20 atm, there were obtained yields of liquid and solid hydrocarbons of 120 g per cu m of $0.6H_2 + 1CO$ and 110 g per cu m of $1H_2 + 1CO$.

Carriers

Kieselguhr. At the Kaiser Wilhelm Institut für Kohlenforschung, precipitated catalysts containing kieselguhr were considered unsuitable for the normal Fischer-Tropsch synthesis. In some tests at the KWI, kieselguhr was incorporated into an alkalized iron catalyst in an attempt to prevent the deposition of carbon upon the catalyst contained in vertical reactors, by diluting the concentration of active metal in the same manner that had been found to be effective in the active cobalt catalysts. A sample of a catalyst containing 40 per cent of kieselguhr, added during evaporation of the catalyst on the water bath, and 1 per cent of K_2CO_3, both based on iron, was tested at 15 atm of $3CO + 2H_2$ and 235°C. It was more durable, as indicated by the gas contraction, than a similar catalyst containing no kieselguhr. However, it was not as satisfactory as the normal iron catalyst because the gaseous hydrocarbon fraction was high and the paraffin wax low. Table 68 summarizes the comparable data for these tests.[102] The catalyst that contained kieselguhr produced less olefinic + oxygenated material (soluble in P_2O_5-H_2SO_4) in the C_2–C_4 and -180°C oil fractions than a kieselguhr-free catalyst. The values for the kieselguhr-free and kieselguhr-containing catalysts were 80 and 35 volume per cent, respectively, in the C_2–C_4 fraction; and 65 and 38 volume per cent, respectively, in the -180°C oil. In the higher-boiling fraction (>180°C) from the catalyst containing kieselguhr there was less oxygenated material than was ob-

[123] C. C. Hall, private communication.

tained from a kieselguhr-free catalyst containing an equivalent quantity of alkali (see Table 53). The kieselguhr-containing catalyst produced approximately 13 g of reaction water, per cu m of $3CO + 2H_2$ gas, in which acetic acid and ethyl alcohol were identified. The latter substance accounted for about 7.5 per cent of the total reaction water. No formic acid and little methyl alcohol were present.

TABLE 68. KWI STUDY ON THE EFFECT OF KIESELGUHR IN PRECIPITATED IRON CATALYSTS (SYNTHESIS AT 235°C AND 15 ATM OF $3CO + 2H_2$ CONTAINING 8–10 PER CENT OF INERTS)

Kg	K_2CO_3, per cent of Fe	Contraction, per cent [a]												C_2+, g per cu m [b]	Hydrocarbon-Products Distribution, weight per cent		
		Days															
		1	2	5	6	8	9	10	20	30	40	50	60	100		C_2–C_4	Liquid	Paraffin [c]
No	0.25	47	50	50	..	..	..	51	55	56	54	54	..	53	148	18	56	26
No	1	45	45	45	..	..	..	52	48	48	47	..	..	..	157	11	47	42
Yes	1	54	54	54	54	56	55	54	54	52	52	50	50	..	123	29	63	8

[a] Includes CO_2.
[b] Grams per cubic meter $3CO + 2H_2$, average of first month.
[c] Determined by butanone method.

U. S. Bureau of Mines tests with kieselguhr-containing precipitated iron catalysts showed that the activity was no lower per gram of iron than that of unsupported iron catalysts and that the type of kieselguhr used in preparing the iron catalyst did not influence the activity and product distribution, in contrast to cobalt catalysts. In agreement with KWI tests,[102] U. S. Bureau of Mines tests showed that the product distribution was strongly shifted toward methane and light hydrocarbons. Data obtained in two tests with catalysts containing kieselguhr are compared in Table 69 [124] with those obtained from a control catalyst. Catalyst P3003.24, of which the composition was $100Fe:10Cu:0.5K_2CO_3$, was prepared according to the procedure described on p 238. Catalysts L6005 and L6006 contained the same constituents in the same proportions and in addition 100 parts, by weight of iron, of Filter-Cel and Hyflo-Super-Cel kieselguhr, respectively. In the preparation of these catalysts, the kieselguhr was added to the solution of the metal nitrates before the precipitant was introduced. All three catalysts were inducted and tested under similar conditions. Table 69 shows that large gaseous

[124] R. B. Anderson, unpublished data.

TABLE 69. EFFECT OF KIESELGUHR IN PRECIPITATED IRON CATALYSTS UPON THEIR ACTIVITY AND PRODUCT DISTRIBUTION (U. S. BUREAU OF MINES)

(Induction conditions: $1H_2 + 1CO$, atmospheric pressure, 230°C, 25 hr, hourly space velocity 100; synthesis pressure, 7 atm of $1H_2 + 1CO$ gas.)

Catalyst number	L6005 [a]	L6006 [a]	P3003.24 [b]
Test, X . . .	122	106	101
Catalyst weight, g	22.0	21.8	79.2
Time, weeks	6	7	7
Temperature, °C	261	260	232
Contraction, per cent [c]	63.6	65.4	64.4
Space velocity	100	102	132
Products, g per cu m feed gas			
CH_4	19.7	18.6	6.3
C_1–C_4	59.9	57.6	23.1
C_5+ (av)	44.5	56.0	99.7
C_5+ (max)	51.6	62.6	115.3
C_5+, weight per cent of hydrocarbons	42.7	49.2	81.2

[a] 7–10 mesh granules.
[b] 6–14 mesh granules.
[c] CO_2-free.

hydrocarbon and small oil yields were produced by the two catalysts that contained kieselguhr.

The Ruhrchemie incorporated kieselguhr into all precipitated iron catalysts and considered the absence of kieselguhr in the KWI iron catalysts a disadvantage in large-scale filtration. However, the kieselguhr content was reduced to a minimum in the special catalyst developed for alcohol production, because the presence of kieselguhr reduced the oxygenated content of the products. The explanation for this effect may be that the silica acts as a dehydrating agent. The composition of the Ruhrchemie alcohol-producing catalyst was 100Fe:5Cu:10CaO:5 kieselguhr, alkalized with 3 per cent KOH.[29,35,125] For preparation on a pilot-plant scale, the hot solution of the nitrates (42 kg iron nitrate, 1.17 kg copper nitrate, 1.75 kg calcium nitrate in 120 l water) was added to a boiling sodium carbonate solution (24 kg sodium carbonate in 120 l water). The kieselguhr (0.35 kg) was added, and the mixture was stirred for a few minutes. It was filtered in a filter press, washed with hot distilled water for 30 min, and then partially dried with air for 15 min. The filter cake was repulped in the precipitation vessel with 500 l of hot distilled water, then filtered in the press, washed for 10 min, and dried in air. This treatment was repeated twice. A solution containing

[125] T.O.M. Reel 42, Bag 3,439, Item 22, p 424, Experiment 650.

0.21 kg of KOH per l of water (equivalent to 3 per cent of the iron in the catalyst) was then used to repaste the catalyst, after which the catalyst slurry was passed through the extrusion press three times. The spaghetti-like threads were dried in an oven at 140°C and then broken into 1–3-mm lengths.

A charge of about 5 l of catalyst was reduced in a 6-l-capacity reduction vessel by passage of 28 cu m of a mixture of $H_2 + N_2$ (75 per cent by volume of H_2) per hr at a temperature of 325°C for 24 hr. It was cooled for 1 hr in a stream of nitrogen, previously freed from oxygen by passage over a sample of a reduced cobalt catalyst, and was removed from the reduction vessel in a nitrogen atmosphere. The shrinkage was 30 per cent, bulk density 780 g per l, iron content (density) 726 g Fe per l of catalyst, and reduction value (iron soluble in acetic acid) 85 per cent.

In a 190-hr laboratory test under 10 atm of water gas with recirculation, a fair conversion rate at a low temperature of 180°–206°C was obtained. Within 75 hr, the conversion of $CO + H_2$ (U) was 65 per cent at 206°C; methane, calculated as per cent of U (M_v), was 18; and the use ratio of H_2:CO (X) was 0.67.[35] A summary of these data is shown in Table 70. These conditions remained constant for the next 100 hr, at the end of which methane production rose sharply to 75 per cent. Upon

Table 70. Ruhrchemie Precipitated Iron Catalysts for Production of Alcohols, 100Fe:5Cu:10CaO:5 Kieselguhr

(Synthesis at 10 atm of water gas containing about 10 per cent inerts and hourly space velocity of 100.)

Test	Laboratory	Pilot-plant
Time, days	8	31
Temperature, °C	180–206	200–214
Conversion of $CO + H_2$, per cent (U)	65	60–65
CH_4, per cent of U (M_v)	18	14
Use ratio, H_2:CO (X)	0.67	0.65–0.72
C_2+ products, g per cu m $CO + H_2$	.....	95
C_5+ products, g per cu m $CO + H_2$	.....	80
Composition of C_5+ products, weight per cent		
Gasoline, <200°C	69.0	60
Oil, 200°–320°C	20.9	12
Wax, >320°C	8.6	28
Olefins + oxygenated compounds, volume per cent [a]		
<200°C	85 [b]	75
200°–320°C	82	70

[a] Soluble in sulfuric acid-phosphoric acid mixture.

[b] Product collected between 81st and 152nd hr of test.

removal from the reactor, the catalyst contained a large amount of carbon. The distribution and properties of the oxygen-containing compounds obtained in this test are shown in Table 71. Total oxygenated compounds in the gasoline fraction comprised 61 per cent of the fraction, in the diesel oil fraction 72 per cent, and in the wax fraction 63 per cent. Roelen was not sure of the structure of the alcohols produced by this catalyst, but his opinion based upon their melting points was that they were chiefly primary alcohols with a fairly high proportion of branched-chain compounds.

Table 71. Properties of Oil Fractions Obtained in a Laboratory Test of Ruhrchemie Alcohol Catalyst

Fraction	<200°C	200°–320°C	>320°C
Weight per cent of C_5+	69.0	20.9	8.6
Density	0.778	0.811	0.824
Refractive index	1.3950	1.4320	1.4471
Oxygenated compounds, volume per cent			
Acids	0.2	0.1	0.2
Esters	3.6	14.4	25.3
Alcohols	51.8	52.7	33.7
Aldehydes	5.6	5.1	2.8
Total oxygen	61.2	72.3	63.1
Olefins, per cent	30.0	28.5	24.2
Total oxygenated compounds + olefins, volume per cent	91.2	100.8	87.3
Fraction soluble in H_2SO_4-H_3PO_4, volume per cent [a]	85	82	....

[a] These values were lower than the sum of the values for olefins + total oxygenated compounds.

Data obtained in a 750-hr pilot-plant test of this catalyst, prepared as described above, and showing a reduction value of 71.8 per cent, are summarized in the second column of Table 70. The wax fraction was larger than was produced in the laboratory test, and the fraction containing olefins + oxygenated compounds was smaller. This catalyst was evaluated as a high alcohol- and olefin-producing catalyst, with a pronounced tendency toward methane production.

One of the early Ruhrchemie iron catalysts had the composition 100Fe:5Cu:30CaO:100 kieselguhr.[29] It was prepared on a semi-technical scale as follows: A solution made up to contain 6 kg Fe and the correct proportion of copper and calcium in 120 l of distilled water was heated to boiling. At the same time, a solution containing 22 kg of sodium carbonate dissolved in 190 l of distilled water was heated to boiling. A quantity of 6 kg of kieselguhr was stirred into the sodium car-

bonate solution and the mixture was boiled for 30 sec. The solution of the metals was then quickly (in 2 min) added with rapid stirring. An additional quantity of 3 kg of sodium carbonate was added to the mixture and stirring continued for 20 sec. The precipitate was filtered in a filter press and washed for 30 min with hot distilled water. The filter cake was put through an extrusion press, which produced very hard granules.

With water gas containing 13 per cent inert constituents, the results shown in Table 72, column 2, were obtained for synthesis at 20 atm and temperatures of 246°–280°C. At an hourly space velocity of 100, for example, and a temperature of 246°C, the conversion (U) was 72 per cent, the yield of C_2+ hydrocarbons was 114 g per cu m of $1H_2 + 1CO$, and the gasoline fraction boiling below 200°C was 33 per cent by weight of the C_5+ hydrocarbon product.

Another catalyst, of which the composition was 100Fe:5Cu:10CaO:150 kieselguhr, was successfully operated by Ruhrchemie at about 250°C. It was to be used in a normal double-tube type of medium-pressure reactor constructed to withstand 25 atm of gas pressure and 50 atm of steam pressure in the plant designed for the Societa Italiana Carburanti Sintetici at Arezzo.[29,39] The catalyst was precipitated from the nitrate by potassium hydroxide solution by a procedure similar to that described on the preceding page.[29] After reduction in dry hydrogen for 1 hr at 300°C, synthesis was carried out at 20 atm of water gas, with a recirculation ratio of 2.5, and an hourly space velocity of 90. During an experiment of 120 days, the temperature was raised from 251° to 257°C. Data obtained in a single-stage, 0.1 full-scale (1,000 l of catalyst), experimental run are shown in Table 72, column 3. This was a wax-forming catalyst, the C_5+ hydrocarbon products containing 36 per cent wax, of which about half was hard wax boiling above 460°C. In a two-stage pilot-plant operation designed to yield an 83 per cent conversion, the production of liquid and solid products was 115 g per cu m of $1H_2 + 1CO$ gas; calculation showed that this yield could be increased to 140 g by operating at 93 per cent conversion and changing the catalyst every 4 months. Subsequently, the precipitant potassium hydroxide, which was expensive, was replaced by sodium carbonate. Sodium salts were washed out after precipitation, and a little potassium carbonate or hydroxide was incorporated into the washed precipitate. A catalyst prepared in this manner produced as little methane as a catalyst precipitated with potassium hydroxide.

When the potassium hydroxide-precipitated catalyst was operated with water gas at 15 atm and a temperature of 225°–250°C, higher wax yields were obtained.[126] In a two-stage pilot-plant operation designed

[126] F.I.A.T. Reel K21, Frames 858–62, March 1941.

TABLE 72. TESTS OF SOME RUHRCHEMIE IRON PRECIPITATED CATALYSTS

1	2			3	4				
Fe-Cu-CaO-kieselguhr	100:5:30:100			100:5:10:150	100:5:8:30				
Process conditions									
Time, days	.....			120	30	30	30	30	40
Pressure, atm	20			20			10		
Temperature, °C	246	267	280	251–257	200–218	218–220	220	220	220
Gas, H_2:CO	1.22 [a]	1.19 [a]	1.23 [a]	1.27 [a]			1		
Recycle ratio, residual:fresh	2.7	2.4	2.0	2.5			2.2		
Hourly space velocity	100	200	284	90					
Contraction, per cent	.....	.....	.....	52	.....	.....		.....	.....
Conversion CO + H_2, per cent (U)	72	68	69	.....	63	64	66	64	62
CH_4, per cent U (M_v)	.....	.....	.....	.....	7.0	6.6	6.8	8.8	8.9
CH_4, per cent of CO converted	6.10	8.10	15.6	.....	3.6	3.5	3.7	4.6	4.7
$C_1 + C_2$, per cent of CO converted	.....	.....	.....	11.0	.....	.....	.....	.....	.....
CO_2, per cent of CO converted	.....	.....	.....	26.8	.....	.....	.....	.....	.....
Utilization ratio, H_2:CO (X)	1.14	1.11	1.13	1.23	1.04	1.14	1.17	1.11	1.12
Yields, g per cu m $1H_2 + 1CO$ gas									
C_2+	114	96	76	.....	105	107	111	104	102
C_5+	.....	.....	.....	103	.....	.....	.....	.....	.....
$C_3 + C_4$	.....	.....	.....	13.5	.....	.....	.....	.....	.....
Composition C_5+, per cent by weight (olefins + O-compounds, volume per cent of fraction) [b]									
Gasoline, <200°C	33	41	62	46 [c] (66)	16.5(44.8)	15.4(30.9)	13.3(28.0)	19.8(48.7)	25.1(66.3)
Oil, 200°–290°C	..	..	..	18 (52)	11.8(46.9)	5.9(42.6)	7.5(38.4)	8.5(52.8)	11.8(64.2)
Soft wax, 290°–320°C	..	..	..		4.1(44.7)	3.7(44.6)	4.6(39.0)	3.8(54.5)	6.0(66.8)
Soft wax, 320°–460°C	..	..	..	19	27.9	27.2	22.9	22.3	25.5
Hard wax, >460°C	..	..	..	17	39.7	47.8	51.7	43.6	31.6
Hard wax, >290°C	..	..	..	..	71.7	78.7	79.2	69.7	63.1

[a] Contains 13.7 per cent inerts.

[b] Soluble in sulfuric-phosphoric acid mixture.

[c] OH number = 24.

to yield 90 per cent conversion of CO, it was posssible to obtain a yield of 170 g of C_3+ products, per cu m of feed gas. The distribution of the liquid and solid fractions was reported as follows: gasoline, <200°C, 15 weight per cent; oil, 200°–320°C, 15; paraffin, >320°C, 70. The >320°C fraction consisted of about 25 per cent soft paraffin and 75 per cent hard wax, and it was pure white. Over an operating period of 2.5 months, the average paraffin yield was 60 per cent. The gasoline and oil fractions were colorless. In these fractions the olefins + oxygenated compounds (soluble in H_2SO_4-H_3PO_4 mixture) comprised 72 and 65 volume per cent, respectively, and the olefins (determined by iodine-thiocyanate) 57 and 47 volume per cent, respectively.

The most active iron Ruhrchemie catalyst reported by Roelen for the medium-pressure synthesis in the commercial reactors was of the following composition: 100Fe:5Cu:8CaO:30 kieselguhr, impregnated with 3–3.5 per cent of KOH. It was prepared as follows:[29,35,39,46] A solution of iron, copper, and calcium nitrates was made up to contain 50–55 g Fe per l and Fe:Cu:CaO in the ratios 100:5:10, the 2 per cent excess CaO being present because it was incompletely precipitated during preparation of the catalyst. The solution of mixed nitrates was prepared in an acid-resistant vessel provided with heating and cooling coils and an effective stirrer, and containing the calculated amount of technical-grade nitric acid (50 per cent HNO_3). The copper, obtained as waste metal in the form of clippings of sheets, wire, etc., was dissolved first in the cold and then at 60°–70°C. Addition of iron turnings in several portions raised the temperature to 80°C. Next, the calculated quantity of calcium oxide in the form of finely divided calcium carbonate, quick lime, or hydrated lime was added slowly, after which the solution was heated to boiling and boiled for several hours. Prepared in this way, the solution was stable and contained, in grams per liter, 115–125 Fe, 5–7 Cu, 11–13 Ca, and no excess of nitric acid. If the iron and lime were free from insoluble impurities, the solution could be used directly. Otherwise, filtration, a troublesome operation because of the usually gelatinous character of the impurities, was necessary.

Precipitation was effected within a period of 5 min by introducing with vigorous stirring the nitrate solution, diluted to reduce the concentration of iron to 50–55 g per l and heated to 98°C, into a boiling solution of the precipitant which contained 90–100 g of Na_2CO_3 per l. The *p*H at the end of precipitation was 6.8–7.0, determined hot with indicator strips (Folienkolorimeter). Stirring was continued for 30 sec longer, and then the calculated amount of kieselguhr, specified to be of low density and roasted at 700°C, was stirred in. The slurry was filtered rapidly in an iron filter press and washed with hot (70°–80°C)

distilled water until the calculated content of sodium nitrate in the finished catalyst was 0.4–0.7 per cent, based on the iron content. More complete washing was unnecessary and, in fact, lowered the desired calcium oxide content. Usually, 200–220 l of water per kg iron in the cake was sufficient. The wet filter cake was made up into a slurry by repulping it in a solution containing 6 g KOH per l, in order to achieve in the moist filter cake produced by a subsequent additional filtration a concentration of 3.0–3.5 g potassium hydroxide per 100 g iron. Shaping the filter cake into 2.5–mm Fadenkorn granules, which were subsequently dried at 110°C, produced a hard catalyst which was resistant to abrasion.

The catalyst was reduced at atmospheric pressure and 300°C for 1 hr with a mixture of 75 per cent hydrogen and 25 per cent nitrogen at an hourly space velocity of 5,000. Reduction was most satisfactory when the catalyst was present in layers 25 cm deep and when the gas flow was high (about 2,000 cu m per sq m cross section per hr). The content of metallic iron after reduction did not exceed 8 per cent and the metallic iron plus ferrous iron did not exceed 60–70 per cent of the total iron present. After reduction, the catalyst was cooled in nitrogen; it was saturated with carbon dioxide slowly, because heat was liberated during this procedure, contrary to the behavior of cobalt catalysts.

The results of a 160-day test with 5 l of this catalyst (3.1 kg catalyst containing 270 g Fe per l) are presented in Table 72, column 4. At 10 atm of water gas with a recycle ratio of residual gas:fresh gas of 2.2:1, its activity was still high at 220°C. The average conversion of $CO + H_2$ (U) was 63 per cent; the methane production (M_v), as percentage of total $CO + H_2$ converted, was 7 per cent; and the utilization ratio of H_2:CO (X) was 1.1. The average yield of C_2+ products was 106 g per cu m $1H_2 + 1CO$. The C_5+ hydrocarbon product contained 68 per cent wax (br >320°C) of which 63 per cent was hard wax boiling above 460°C.

Comparing the wax yields from iron and cobalt catalysts, Roelen suggested the following values for the hard wax (br >460°C): normal-pressure cobalt 3 per cent, medium-pressure cobalt 25 per cent, iron 50 per cent of the total product. The presence of oxygen compounds probably made the waxes from iron catalysts more plastic and more similar in properties to natural ceresin, but Roelen did not think they had as yet been tested for industrial purposes.

When interrogated in 1945, Roelen [35] stated that the costs of manufacture of iron catalysts had been reduced by the use of sodium carbonate as precipitant in place of potassium carbonate. High kieselguhr contents increased the cost of iron catalysts, but a less pure kieselguhr might be used, as the impurities, such as iron and calcium, obviously had no

deleterious effect on iron catalysts. It was intended to regenerate iron catalysts by a wet process, using dilute nitric acid, which would dissolve the copper and 80 per cent of the iron, but the process had not been fully developed, particularly from the point of view of the impurities likely to be present, *eg*, Al and Pb. The recovery of copper and the calcium was believed worth while. Solution of the last 20 per cent of the iron was thought probably uneconomic.

A catalyst used by the Ruhrchemie toward the end of World War II for operation at atmospheric pressure and low temperature was described by Roelen.[35] Its composition was 100Fe:5Cu:10CaO:100 kieselguhr, and it contained 240 g Fe per l. When reduced with hydrogen, this catalyst produced a large amount of methane, but pretreatment with water gas decreased this fraction. Synthesis began at 140°C and produced a low conversion of $CO + H_2$ of about 50 per cent and a low use ratio of H_2:CO of 0.8–0.9. The products had a low boiling range.

The catalyst developed by Rheinpreussen in 1944 for atmospheric-pressure synthesis had the composition 100Fe:(1–10)Cu:(0.5–1.5)K_2CO_3:(50–100) kieselguhr and depended for its success upon a special pretreatment procedure.[29] This catalyst was prepared by dissolving the iron in nitric acid to give a 10 per cent solution, adding the copper nitrate, boiling, adding the kieselguhr, precipitating with boiling 10 per cent sodium carbonate solution, filtering, and washing. The alkali dissolved in water was stirred into the filter cake, which was dried and broken into 1–3-mm granules. The catalyst was pretreated at atmospheric pressure of $1CO + 2H_2$ gas carefully freed from both carbon dioxide and water vapor and passed at 20 times the normal synthesis gas rate either directly or with recirculation (recirculation ratio 3). Synthesis was carried out at atmospheric pressure of water gas with recirculation, or of a gas richer in hydrogen, approaching the composition of $2H_2 + 1CO$, without recirculation. The longest test without reactivation was made with water gas for 2 months at 218°C, at the end of which time the catalyst was still active. It was estimated that the catalyst lifetime would be at least 4 months. For one stage at an hourly space velocity of 250, the yield of C_1+ products was 130–135 g per cu m $1H_2 + 1CO$ gas, and for two stages at a total hourly space velocity of 100, it was 160 g per cu m or 10 g CH_4 + 150 g of C_2+ products. Half of the oxygenated product was water and half carbon dioxide. The use ratio of H_2:CO (X) was about 1. Carbon monoxide conversion (U_{CO}) was 85–90 per cent for stage 1 and 97 per cent for the two stages together. The wax fraction was similar to that obtained from the cobalt medium-pressure synthesis, and the amount of olefins in the total product (40–50 per cent) was much higher.

A precipitated iron Lurgi catalyst of composition 100Fe:(5–10)Cu: $9Al_2O_3$:120 kieselguhr was used in a process primarily intended for the detoxification of town gas produced by the Lurgi pressure-gasification process.[39, 127] Single-stage treatment over this catalyst, without recirculation of the gas, at 20 atm and 250°–280°C was reported to leave only 5–8 per cent of CO in the gas. A few runs were made in a pilot plant erected at the A.G. Sächsische Werke, Böhlen, near Leipzig. The unit consisted of a normal Fischer-Tropsch tube- and plate-type assembly enclosed in a cylindrical vessel, and it contained about 6 cu m of catalyst. Passage of Lurgi gas, containing 17 per cent CO and free from sulfur compounds, through the unit at 1,600 cu m per hr produced 30–40 g of liquid product per cu m of input gas. The composition of this product was as follows, in weight per cent: gasoline 25–30 (olefins 50–60 per cent), Diesel oil 10–30, soft wax 20–30, hard wax 25–30. The octane number of the gasoline fraction was 70, and the cetane number of the Diesel oil fraction 65.

Luxmasse and Lautamasse. A Lurgi catalyst, designed for the production of high yields of olefins and hydrocarbons in the gasoline range, was prepared by impregnating Lautamasse with copper.[38, 127, 128] Lautamasse was the iron oxide residue resulting from the alkaline extraction of bauxite during the manufacture of aluminum. It had the following approximate composition: 50 per cent Fe_2O_3, 11–12 Al_2O_3, 3–4 Na_2O, 7–8 TiO_2, 4–5 SiO_2, 8–9 CaO, 1–2 MgO, 0.1–0.2 MnO, 0.8–1.0 SO_2, 0.3–0.8 P_2O_5, 50–55 H_2O. The Lautamasse was wetted with a quantity of copper-ammonium nitrate solution calculated to produce a final copper content of 3 per cent. The copper was then precipitated on the carrier with K_2CO_3 and the catalyst reduced by hydrogen (conditions not given). This was not a highly active catalyst and required a high operating temperature of 275°C. Less deterioration due to carbon deposition was observed than would have occurred with a more active catalyst. The synthesis was carried out in the conventional-type, externally cooled, medium-pressure reactor, as built by Guttenhoffnungshutte, at 20 atm of $1.6CO + 1H_2$ gas at an hourly space velocity of 100, and an hourly recycle-gas space velocity of 300. Only one stage was required, in which the conversion was 85 per cent. The total yield, per cu m $CO + H_2$, was 135 g, including 98 g C_5+ hydrocarbons, 32 g $C_3 + C_4$ hydrocarbons, and 5 g alcohols. In addition, there was produced 35 g of $C_1 + C_2$ products per cu m $CO + H_2$ gas. The product

[127] C. C. Chaffee, O. F. Thompson, J. G. King, H. V. Atwell, and I. H. Jones, PB 12,624 (1945), 54 pp; C.I.O.S. File XXXI-23, Item 30.

[128] H. Hollings and J. G. King, PB 4,328 (1945), 12 pp; C.I.O.S. File XXXII-91, Item 30.

distribution of the liquids plus solids, in weight per cent, was as follows: 71 gasoline (<200°C), 21 Diesel oil (200°–320°C), and 8 soft wax (320°–460°C). The olefin content of the gasol ($C_3 + C_4$) fraction was 70 volume per cent; of the gasoline, 75; and of the Diesel oil, 60.

Promising catalysts consisting of Lautamasse and alkali carbonates were reported at Brabag.[38,39] High operating temperatures of 250°–270°C with CO-rich gas ($0.6H_2 + 1CO$) at 10–15 atm were used. One such preparation containing 5–6 per cent of K_2CO_3 produced an average yield of 146 g C_2+ hydrocarbons per cu m $H_2 + CO$ gas, at 246°C, over a period of 3 months. The products contained 70–80 per cent olefins and the octane number (research) of the 38°–160°C fraction was claimed to be 82.

A Ruhrchemie catalyst developed in 1940 in an attempt to make catalysts hard enough for use on a large scale was deposited on Luxmasse.[29] Luxmasse was similar in composition to Lautamasse but contained 15 per cent of Na_2O instead of 3–4.[31] The composition of the catalyst was 100Fe:3.5Cu:100 bleaching earth:10 kieselguhr. In its preparation, a volume of 1,100 cc of 10.3 per cent KOH solution, specific gravity 1.085, was heated to boiling; 3.5 g kieselguhr S.120 was added, and the boiling continued for 1.5 min. Then, with continuous and vigorous stirring, a suspension of 200 g Luxmasse (35 g Fe), 35 g bleaching earth (Granosil), and 10.3 cc copper nitrate solution (1.25 g Cu) in 500 cc hot distilled water was added. Heating and stirring were continued until the mixture was brought to the boiling point. It was filtered and washed 3 times with 200-cc portions of hot (90°C) distilled water; the filter cake dried at 110°–115°C. After granulation, the bulk density was 500 g per l.

Synthesis was started with water gas at atmospheric pressure, at an hourly space velocity of 100, and the temperature was increased until the contraction was 20 per cent. The pressure was increased to 15 atm and the temperature to 255°C. The recirculation ratio (residual gas: feed gas) was 1.5–2.5:1. The use ratio of H_2:CO (X) was 1.27, and the conversion of $CO + H_2$ (U) 60 per cent. The yield calculated for a 90 per cent conversion was 95 g C_5+ hydrocarbon products and 21 g C_2–C_4 products per cu m $H_2 + CO$ gas. The distribution of the liquid product was as follows, in weight per cent: 39 gasoline (<200°C), 31 Diesel oil (200°–320°C), and 30 wax (>320°C). The gasoline fraction had an octane number of 72. This catalyst was unsatisfactory because it required a high synthesis temperature.

At Rheinpreussen, Luxmasse and Lautamasse produced fairly active catalysts which, however, required high synthesis temperatures.[129] A

[129] F.I.A.T. Reel 116-X, Frames 1,717–87, 17th Communication.

125-day test in the gas phase at 10 atm of CO-rich gas (probably $2H_2 + 3CO$) produced at 248°C a yield of 164 g, excluding methane, per cu m $H_2 + CO$ gas. The catalyst consisted of Luxmasse which had been dried, washed to remove soluble impurities, and alkalized.

Dolomite. Dolomite was considered by Rheinpreussen to be satisfactory as a carrier for promoting wax production, preventing carbon formation during pretreatment, and producing a hard catalyst. Material from a band of dolomite selected to be free from sulfur and phosphates was roasted at 700°C and then finely powdered. A synthetic dolomite consisting of an equimolar mixture of magnesium and calcium carbonates produced somewhat less active catalysts.

Carriers were incorporated into Rheinpreussen catalysts in 1941, when the cobalt supply in Germany became critical and the emphasis in Fischer-Tropsch synthesis shifted to high wax production. The Rheinpreussen iron catalysts precipitated on carriers were to be used in the conventional gas-phase synthesis. Experiments with Rheinpreussen catalysts precipitated on dolomite in the liquid-phase medium showed no improvement over the results obtained with carrier-free catalysts.[130] For example, a catalyst precipitated on dolomite and alkalized with 3 per cent of K_2CO_3 produced much poorer results than the normal, alkalized, carrier-free preparation.

The iron catalyst described by Kölbel as the best one developed at Rheinpreussen for the gas-phase, medium-pressure synthesis was precipitated on dolomite.[29,107] Its composition was 100Fe:(1–10)Cu:(50–100)dolomite:(0.1–3)K_2CO_3. In the preparation of this catalyst, iron was dissolved in a slight excess (5–10 per cent) of dilute nitric acid to give a 10 per cent solution, the temperature rising to about 50°C during this period. Copper nitrate was added, the solution heated to boiling, powdered dolomite added, and the precipitation carried out by adding boiling 10 per cent sodium carbonate solution. The excess of sodium carbonate used was as small as possible, so that a considerable amount of magnesium remained in solution. It was thought essential that the procedure be carried out in the order given. Filtration was carried out immediately, followed directly by washing until the filtrate was free from NO_3^-, by the brown ring test. This took about 45 min for a laboratory-scale preparation, the filter funnel being refilled with fresh water 6 or 7 times. An aqueous solution of potassium carbonate was stirred into the wet filter cake, which was then dried and broken. Granules 1–3 mm in size were collected. The catalyst was not formed by extrusion through dies. Kölbel reported that a successful prepara-

[130] F.I.A.T. Reel 116-X, Frames 1,593–630, 12th Communication.

tion had been carried out on a large scale in the Brabag catalyst factory, the filtration being easier than for the normal cobalt catalyst.

Pretreatment was a critical step. It was done in 3–24 hr at atmospheric pressure and at 280°–320°C with $2H_2 + 1CO$ gas carefully freed from carbon dioxide but not dried. The gas was recirculated in the proportions of 9 parts of recycle gas to 1 part of fresh gas, the total minimum space velocity being 1,000 volumes of gas per volume of catalyst per hour. The pretreatment time required was judged by following the evolution of CO_2. As shown in Figure 40,[107] CO_2 concentration in the gas increased to a maximum, possibly as a result of decomposition of metallic carbonates, then fell to a minimum, and again slowly increased to a second maximum during carbide formation. Ideally, the pretreatment was concluded when the second maximum was reached (curve *A*). If carbon formation occurred, a curve similar to *B* was obtained and the catalyst was usually inactive.

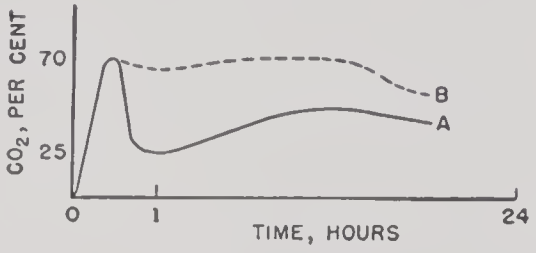


FIGURE 3–40. Pretreatment of iron catalyst for the Rheinpreussen gas-phase medium-pressure synthesis. Reproduced from reference 107.

The temperature at the end of pretreatment was decreased and synthesis started at 205°C and 10 atm of $2H_2 + 1CO$ gas. Kölbel [107] advocated operation with two or preferably three stages, or with recirculation of the residual gas. With three stages, a CO conversion of 90–95 per cent could be obtained with an overall space velocity of 150, *ie*, twice that used in the normal technical-scale plants. As an example of the performance of such a catalyst, Kölbel quoted data for a test made under the above conditions. The temperature rose from 205° to 215°C, but the catalyst life could not be determined because the run was terminated by bombing after 1,200 hr. The use ratio of H_2:CO was 1.5. The yield, including methane, was 159 g per cu m $2H_2 + 1CO$ gas. The methane fraction was about 5 per cent of the total product; this was less than that produced in the cobalt medium-pressure synthesis. The products were similar to those obtained from cobalt catalysts at atmospheric pressure, particularly with respect to the small wax fraction. The wax fraction could be increased by using more alkali in the catalyst, or by operating at higher pressure, or by using a higher proportion of carbon monoxide in the synthesis gas. However, $2H_2 + 1CO$ gas was preferable to $1H_2 + 1CO$ gas (1) in preventing carbon formation; (2) in producing less carbon dioxide, the presence of which hindered recovery of product by adsorption on active carbon; (3) in

producing wax more suitable for oxidation; and (4) in lowering synthesis temperature by about 15°C.

Silica. Another carrier used in precipitated iron catalysts, particularly by Lurgi Gesellschaft für Warmetechnik, was silica. Herbert (Research Director of Lurgi) described the following as the best iron catalyst for medium-pressure synthesis that was developed in his laboratory: $100Fe:25Cu:9Al_2O_3:2K_2O:30SiO_2$.[29,127,128] This catalyst was prepared by dissolving copper and aluminum nitrates in a 10 per cent solution of ferric nitrate in sufficient quantities to produce the specified ratio of metals. The solution was heated, and a 10 per cent solution of sodium carbonate was added rapidly at about 70°C in the quantity required to precipitate the metals. Freshly prepared silica, obtained from water glass and dilute mineral acid, was added rapidly and the mixture stirred for about 1 min. The slurry was then filtered, washed to a *p*H of 8.0, and impregnated with the requisite potassium carbonate equivalent to 2 per cent K_2O. The preparation was dried in a centrifuge until it could be extruded and was further dried on a conveyor belt by a blast of hot air to facilitate cutting up the spaghetti-like threads into desired lengths. Final drying was carried out at 100°C. The alkali silicate, *ie*, K_2O plus equivalent amount of silica, was responsible for the good mechanical strength and long life. It was thought that its function was to stabilize the paste during preparation of the catalyst and prevent thixotropic liquefaction. As a result, the dry catalyst threads were hard and glassy when broken.

Pretreatment in practice was carried out in the synthesis unit with hydrogen at an hourly space velocity of 1,000 for 1–3 hr, at 250°–300°C, the exact time and temperature depending upon the alkali and copper content. High alkali contents required longer reduction periods. The catalyst containing 25 per cent copper could be reduced at 250°C.[29,39,127]

Synthesis was carried out on a laboratory scale at Mousson Strasse and on a pilot-plant scale at Hoesch-Benzin, Dortmund.[38,39,127] The latter was a conventional-type, externally cooled, double-tube, medium-pressure reactor as built by Guttenhoffnungshutte, and was operated with a low recycle ratio (2.5:1) in stage 1. The synthesis was started at 20 atm of water gas containing less than 10 per cent inerts and an hourly space velocity of 100. The starting temperature of 180°C was raised to 220°C in 2 days. Over an operating period of 3 months, the temperature was raised to 230°C. Such a catalyst had not been run to exhaustion by Lurgi, but it was believed that its life would be about 1 year. This was intended primarily as a wax-producing catalyst, from which a yield of C_3+ hydrocarbon products of 136 g per cu m $1H_2 + 1CO$ gas was obtained in stage 1, and a total yield of 170 g, including 15 g $C_3 + C_4$, 9 g alcohols, and 146 g C_5+ hydrocarbon products, per cu m

$1H_2 + 1CO$ gas, was calculated for two stages. The calculated $C_1 + C_2$ fraction was 18 g per cu m. The distribution of the C_5+ hydrocarbon fraction was as follows: gasoline, <200°C, 20 weight per cent; Diesel oil, 200°–320°C, 20; soft wax, 320°–460°C, 15; and hard wax, >460°C, 45. The olefin content, in volume per cent, was as follows: gasol ($C_3 + C_4$), 60; gasoline, 60; and Diesel oil, 45.

A Ruhrchemie catalyst of composition $100Fe:5Cu:100CaO:6.5SiO_2$ was deposited on silica in a manner similar to that used by Lurgi.[131] The nitrates of iron, copper, and calcium were dissolved and heated to boiling in such quantities that the hot solution contained 1.8 kg Fe and the appropriate amounts of Cu and Ca in 50 l of water. This was added to a boiling solution containing 6.4 kg of Na_2CO_3 in 50 l of water. After suction filtration, the filter cake was washed with 72 l of hot distilled water and then suspended in a solution consisting of 50 l of water + 443 cc of a potassium water glass solution which contained 234 g SiO_2 per l. The slurry was refiltered, spread on trays, and collected in 3-mm granules which were dried at 110°C. After reduction with $75H_2$-$25N_2$ mixture at 305°C and an hourly space velocity of 6,000 for 1 hr, the catalyst was tested at 10 atm of water gas, with recirculation. In a 460-hr test, good conversion of $CO + H_2$ (U) was obtained at 214°C (U = 62 per cent), but methane production was high (per cent of U, M_v = 16), and the use ratio of H_2:CO was low (X = 0.71). Roelen [35] stated that iron catalysts were much more difficult to reproduce than cobalt and that differences arising from uncontrolled variations in technique during preparation were sometimes as great as those to be expected from a deliberate variation in the chemical composition of the catalyst. Preparations impregnated with potassium water glass were particularly hard to reproduce, probably because of the non-homogeneous composition of the water glass. It was thought that this difficulty could be overcome by impregnating with KOH or K_2CO_3 and by preboiling a portion (10–50 per cent) of the carrier kieselguhr for a short time with the precipitant, to produce the good effects that Lurgi had achieved by use of water glass in catalysts. However, Roelen [35] admitted that the procedure of preboiling the kieselguhr was abandoned because it produced unknown contents of alkali and silicate.

FUSED, SINTERED, AND CEMENTED CATALYSTS

Fused and sintered iron plus alkali (synthetic-ammonia-type) catalysts were studied at the I.G. Farben. laboratories, following the line of investigations originated by the Badische Anilin und Soda Fabrik. A distinction has been made in the U. S. Bureau of Mines laboratory be-

[131] T.O.M. Reel 42, Bag 3,439, Item 22, p 394, Experiment 725.

tween the type of catalyst in which the active component is drastically modified by heat and that in which the particles of iron oxide are cemented into granules by the addition of aluminum nitrate or other binding agents. The former catalysts should correctly be named "sintered," and the latter, "cemented." Changes that occur in the structure of the iron oxide in the latter catalysts are usually slight. Catalysts of the fused, sintered, and cemented types are at present of particular interest in the more recently developed Fischer-Tropsch processes, the fluidized and oil-circulation techniques. In these processes, catalyst granules of high mechanical strength and resistance to abrasion are necessary. Development of such catalysts, prepared from relatively inexpensive, finely powdered iron oxide, is in progress.

Fused Synthetic-Ammonia-Type Catalysts

German synol catalyst. The first synol catalyst (in 1940) was the Leuna synthetic-ammonia catalyst WK 17.[38,132,133] It was prepared by placing 19 kg of iron from a wood charcoal preparation in a shallow water-cooled iron pan 50 cm in diameter and 15 cm in depth. Pure oxygen, supplied by two nozzles, was directed toward the mass, which melted in 10 min. A quantity of 1 kg of the promoter was added to the molten mass and the oxidation was completed in another 20 min. The promoter was made by dissolving 16 kg of pure Al_2O_3 and 4 kg of KNO_3 in 2 l of 60°Bé nitric acid and 2–4 l of water; this mixture was boiled and cooled to a solidified cake. Sometimes a little lime was also added. The catalyst melt was poured out on an iron pan and allowed to cool slowly. It was broken up into 0.5–1.0-mm granules; the dust was remelted electrically. The following values were reported for the analysis of the Leuna synthetic-ammonia catalyst, in per cent: 97 Fe_3O_4, 2.5 Al_2O_3, 0.2–0.6 K_2O, 0.16 S, and 0.03 C. The apparent or bulk density was 2.0.

For use in the synol process, the catalyst was reduced in batches of about 500 l with pure, dry hydrogen containing less than 0.02 mg of sulfur per cu m, as shown in the simplified diagram of Figure 41, at atmospheric pressure and a temperature of 450°C. Reduction temperature was apparently not critical, as a range of 380°–650°C was stated to be satisfactory. The essential features of the catalyst reduction were reported to be (*a*) a high space velocity of not less than 2,000 l of hydrogen per l of catalyst per hr, and (*b*) efficient drying of the recycle and make-up hydrogen. The recycle hydrogen leaving the reduction vessel

[132] R. Holroyd, Editor, *U. S. Bur. Mines Inform. Circ.* 7,370 (1946), pp 13, 95–6; PB 6,650; *C.I.O.S. Rept.* XXXII-107, Item 30 (1945).

[133] T.O.M. Reel 86, Bag 3,979, Item 78.

contained 1–2 g of water per cu m. It was passed through a water cooler at 20°C, through an ammonia cooler at 4°C, and, after mixing with fresh hydrogen, through a silica-gel dryer. The time required for reduction of a batch of catalyst was about 50 hr. Absence of water in the exit gas was used as a criterion of completeness of reduction. After cooling to 50°C, the reduced catalyst was transferred to small steel containers (Kübel) of 150–200 l capacity, in an atmosphere of CO_2. From these,

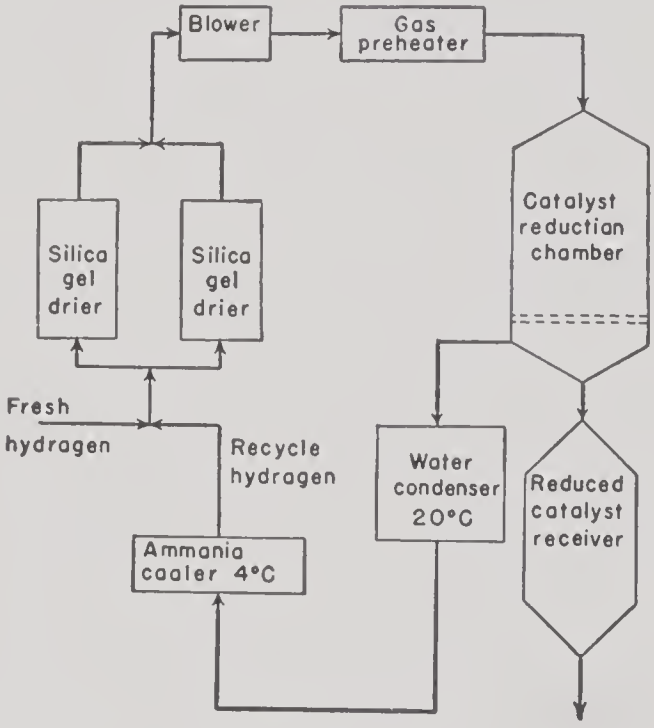


FIGURE 3–41. Simplified diagram for reduction of synol catalyst. Reproduced from reference 132.

the catalyst was charged to the synthesis reactors. Details of the operation of the process and distribution of the products are described in Chapter 4. Reports from Leuna dated 1941 and 1942 [134] indicated that improvement in the catalyst was attempted by remelting unreduced, finely pulverized catalyst WK 17 with carbonyl iron in an oxygen stream. It was believed that the improved homogeneity and porosity of the catalyst produced by this procedure resulted in higher activity.

In studies of the synol catalyst, about 1 per cent Mn_2O_3 or 1 per cent ZnO, based on iron, proved to be less effective as promoter than about 3 per cent Al_2O_3. The addition of a small amount of arsenic in one catalyst (3798) produced 23–25 per cent esters in the 200°–300°C fraction and was suggested as a possible starting point for the development of a catalyst to synthesize esters or acids directly.

[134] T.O.M. Reel 134, *Repts.* 283 and 326.

U. S. Bureau of Mines tests. Some samples of American synthetic-ammonia-type catalysts, the compositions of which are shown in Table 73, were selected for a study of catalysts of high mechanical strength, and these were tested in the Fischer-Tropsch synthesis. A sample of German synol catalyst obtained from the I.G. Farben., Leuna, plant was

TABLE 73. COMPOSITION OF COMMERCIAL SYNTHETIC-AMMONIA CATALYSTS (ANALYSIS BY U. S. BUREAU OF MINES)

Constituent	Per Cent by Weight of Each Constituent in					
	D3001	D3006	D3004	D3005	D3007	D3008
Total iron [a]	66.78	67.95	68.81	70.28	66.79	70.04
Ferrous iron	.....	22.54	.....	26.08	23.62	27.16
Al_2O_3	None	None	2.8	2.79	2.76	1.98
MgO	4.62	4.61	None	None	None	None
Cr_2O_3	0.75	0.65	.....	0.01	0.02	None
Mn_3O_4	0.05	0.03	.....	0.07	0.29	0.05
K_2O	0.61	0.56	1.9	1.46	1.24	0.97
CaO	....	None	.....	None	0.22	0.05
SiO_2	0.62	0.64	0.2	0.14	1.86	0.20

[a] $\frac{100}{\text{total iron}} \times$ other constituent = per cent of other constituent, based on iron.

also tested, in order to obtain comparable results. This catalyst was described as a synthetic-ammonia type of preparation, made by burning iron in oxygen and promoted with aluminum and potassium oxides. It was probably also remelted with carbonyl iron. Its composition, obtained by analysis, was as follows: $100Fe:4.92Al_2O_3:0.94K_2O:2.92CaO$, parts by weight. The synol catalyst tested in X113 was more active than the commercial American synthetic-ammonia catalysts, as indicated by the low operating temperature (219.5°C) and low methane yield (6.0 weight per cent). Later tests, described below, indicated that the small particle size of the synol catalyst was chiefly responsible for its greater activity. A summary of the results of the tests of these catalysts is presented in Table 74.[124] The activity of the synol catalyst increased during the test; the commercial synthetic-ammonia catalysts decreased in activity during synthesis. The catalysts containing magnesia were more active than those containing alumina. The operating temperatures in the tests of catalysts D3001 and D3006 were lower than those of D3004, D3007, and D3008.

TABLE 74. SUMMARY OF TESTS WITH GRANULAR 6–8 MESH AMERICAN COMMERCIAL SYNTHETIC-AMMONIA CATALYSTS AT 7 ATM OF $1H_2 + 1CO$ GAS

(Reduced in dry H_2 for 40–50 hr at 450°C and hourly space velocity of 5,000, except as indicated; inducted and operated at 7 atm of water gas.)

Catalyst	Test, X . . .	Weight Loss on Reduction, per cent	Catalyst-Testing Data										
			Temperature, °C	Contraction, °C	Products, g per cu m feed gas			Distribution of Hydrocarbons, weight per cent				Time, weeks [a]	SVH
					H_2O	CO_2	Hydrocarbons	CH_4	C_2	$C_3 + C_4$	C_5+		
D3001	105 [b]	25.1	256.0	63.2	25.8	323.9	118.8	11.9	8.6	19.4	60.0	5	99.8
D3006	124 [b]	25.8	252.0	61.8	29.2	333.4	113.3	13.7	9.2	18.9	58.2	2	102.5
D3004	114	16.1	298.0	64.8	27.5	304.1	100.2	26.2	8.8	19.3	45.7	1	100
D3005	136 [b]	23.8	261.8	65.5	25.9	328.5	115.7	13.2	8.0	18.8	60.0	5	96.1
D3007	133	16.1	264.5	64.8	17.6	383.2	123.4	13.5	9.3	17.8	59.4	5	97.2
D3008	127	18.5	271.0	64.2	26.9	346.6	115.5	14.9	10.0	20.7	54.4	4	103.5
German synol [c]	113 [b]	14.8	219.5	65.8	17.8	329.6	123.3	6.0	4.9	10.5	78.6	8	86.5
A3212	129	16.7	281.0	65.6	21.6	314.9	109.1	16.1	8.0	21.8	54.1	3	97.0
A3217	148	15.7	265.5	63.5	17.8	346.5	115.7	16.6	10.4	18.7	54.3	4	99.3
A4900	171 [b]	18.0	259.3	64.0	19.9	326.0	116.0	16.3	10.7	20.8	52.2	4	100.5
D3001 [d]	201 [b]	26.5	226.6	64.8	22.9	279.0	113.0	7.1	5.8	14.0	73.1	7	99
L3011	208 [b]	18.8	246.8	65.4	28.5	290.9	104.9	12.3	6.5	19.3	61.9	4	99.5

[a] Continuous operation.
[b] Reduction space velocity was about 2,500.
[c] Fine powder.
[d] 40–60 mesh.

Catalysts A3212, A3217, and A4900 were U. S. Bureau of Mines preparations. The composition of A3212 was $100Fe:3.5Al_2O_3:0.5K_2O$, parts by weight, based on starting materials; this catalyst was made by mixing Al_2O_3 and K_2O with electrolytic iron and burning the mixture in oxygen. Catalyst A3217, of composition $100Fe:5.0Al_2O_3:0.45K_2O$, parts by weight, was made by burning pure iron in oxygen in the presence of aluminum and potassium nitrates. Catalyst A4900, of composition $100Fe:4.92Al_2O_3:0.94K_2O:2.92CaO$, was prepared by the procedure found in the German documents (see p 272) for the synol catalyst. All three catalysts were inferior to the German synol catalyst in test X113, as indicated by the data for tests X129, X148, and X171, but as active as most synthetic-ammonia-type catalysts. Tests X201 and X208 showed that the activity of the commercial synthetic-ammonia catalyst D3001 could be enhanced to a large extent by the use of a smaller particle size and to a smaller degree by remelting of the catalyst and incorporating carbonyl iron into the melt. Catalyst D3001, 40–60 mesh, in test X201 was much more active than the 6–8 mesh granules in X105; the synthesis temperature and methane fraction were lower in X201 than in X105 but similar to the corresponding values in X113. Catalyst L3011, which contained 30 per cent of carbonyl iron fused into D3001, was somewhat more active in test X208 than was D3001 in X105. It is possible that the combined effects of smaller particle size and refusion of the catalyst would make D3001 as active as the German synol catalyst.

Other fused iron catalysts. The experiments of Linckh at Oppau, in which carbon monoxide and hydrogen mixtures at pressures of 100–200 atm were passed over fused iron oxide catalysts, date back to 1926. These tests led to the development in 1935–1938 of the Duftschmid oil-recycle process, which is described in detail in Chapter 4, p 400. In this process, liquid hydrocarbons were obtained at 15–20 atm of CO-H_2 mixtures in the presence of a fixed-bed catalyst consisting of promoted fused iron, the heat of reaction being removed by the vaporization of cooling oil flowing over the catalyst. The most frequently used, standard catalyst (997) was prepared in a manner similar to that used for synthetic-ammonia catalysts. Iron powder in water-cooled crucibles was melted by a stream of oxygen, and the necessary promoters were added to the melt.[70,135,136] For 100 parts of iron powder, 2.5 each of silicon powder and titanium oxide, and 5 each of potassium perman-

[135] E. Linckh and F. Winkler, German Patent 708,512, Nov. 14, 1935; French Patent 812,290; British Patent 465,668.

[136] F. Duftschmid, E. Linckh, and F. Winkler, U. S. Patent 2,159,077, May 23, 1939.

ganate and water, were used. Instead of potassium permanganate, manganese oxide or manganese powder, and potassium hydroxide could be used. The fused cakes, containing iron as magnetite, Fe_3O_4, were crushed to 6–12-mm granules (bulk density 2.5 kg per l) and then reduced in a separate unit with dry hydrogen at a space velocity of 200–300 l per kg catalyst per hr and a temperature of 450°–500°C for 5–6 days. After reduction, the catalyst was strongly pyrophoric and was discharged from the reduction vessel into a container of oil, for transport to the synthesis reactor. In a typical pilot-plant test at 20 atm of $1CO + 0.8H_2$ gas, at a temperature of 240°–290°C in the first stage and 270°–320°C in the second stage, the conversion of $CO + H_2$ (U) was 90 per cent and the yield of C_3+ products was 145–150 g per cu m ($CO + H_2$). More than 60 per cent of the total C_3+ product was a highly olefinic oil boiling below 320°C, as shown by the data in Table 75. The primary

Table 75. Distribution of C_3+ Product from Duftschmidt Oil-Recycle Process over Fused Iron Catalyst

Fraction	Distribution, weight per cent	Olefins, volume per cent
$C_3 + C_4$	14	80
<100°C	19	50–65
100°–150°C	11	40–55
150°–175°C	4	35–45
175°–325°C	19	20–35
325°–400°C	11	20
>400°C	17 [a]	..
Alcohols	5 [b]	..

[a] Hard paraffin melted over 90°C.
[b] Soluble in H_2O.

gasoline had a research octane number of 65, which was increased to 85 by the addition of 0.1 per cent tetraethyllead. The middle-oil fraction was readily usable as Diesel fuel; a typical analysis was as follows:

Specific gravity at 15°C, kg per l	0.809
Flame point, °C	66
Pour point, °C	−9
Viscosity at 20°C (Engler)	1.70
Cetane number	75.5
Conradson test, per cent	0.3

A U. S. Bureau of Mines test was made of a similar iron catalyst, of composition $100Fe:2.5Si:2.5TiO_2:5KMnO_4$. The catalyst was reduced by hydrogen at 500°C, passed for 48 hr at a space velocity of 5,000, and

was inducted with $1H_2 + 1CO$ gas at 7 atm while the temperature was raised 7°C per hr until the contraction was 63 per cent. When tested for 4 weeks at 247°C, a pressure of 21 atm of $1H_2 + 1CO$ gas, and a space velocity of 300, the yield of hydrocarbon products, in grams per cubic meter of feed gas, was as follows: 13.8 CH_4, 45.7 C_1–C_4, and 70.8 C_5+.[124]

Another German catalyst, prepared by fusion in a stream of oxygen, had the following composition, in per cent: 89.5 iron powder, 2.24 titanium dioxide, 2.24 silicon powder, 2.24 manganese oxide, 2.03 copper powder, and 1.8 potassium hydroxide dissolved in water. The molten catalyst cakes were crushed to small particles and reduced at 650°C with hydrogen passed at a space velocity of 500–700 l per l catalyst per hr for 3 days. This catalyst was designed for high ethyl alcohol production in a high-pressure gas-recycle process developed at I.G. Farben., Oppau, by Klemm and Linckh.[70,137] Part of the catalyst charged into the synthesis reactor (upper 16 per cent of the reactor space) was treated with slightly acidified 5 per cent copper nitrate solution, which was reported to prevent carbon formation at the inlet portion of the converter. Synthesis was carried out in an externally cooled, double-tube type of reactor, containing a catalyst annulus of 10–12 mm, at a temperature of 290°–320°C, a pressure of 180 atm, and a recycle ratio of residual:fresh gas of 3:1. Synthesis gas was rich in hydrogen, the average $CO:H_2$ ratio being about 1:3.5. An average yield of C_3+ products of 53.3 g per cu m $CO + H_2$ was distributed as follows: $C_3 + C_4$, 8.5 weight per cent; hydrocarbons, 41.5; alcohols, 50. About half of the total yield consisted of alcohols, of which 50 per cent was soluble in water and was recovered from the reaction water. The crude alcohol solution, containing about 10 per cent water, consisted of the following products, in per cent:

Acetaldehyde	2–3
Acetone	3–5
Methanol	10–15
Ethanol	60–70
Higher alcohols	10–15

Petrographic studies of fused iron catalysts described in the preceding pages were made at Oppau in 1944.[138] It was observed that the more active catalysts for the Fischer-Tropsch synthesis contained the simplest macro structure. In such catalysts, most of the iron was present as magnetite (Fe_3O_4) and the promoters were almost entirely in solid solution in the magnetite phase. The more basic the catalyst, the more it

[137] R. Klemm, E. Linckh, and F. R. Winkler, German Patent 76,490, Dec. 20, 1943.

[138] T.O.M. Reel 278, Fused Iron Catalysts for CO-H_2 Syntheses, Oppau (July 1, 1944), 44 pp.

tended to produce solely hydrocarbons; with more acidic constituents, alcohol and other oxygenated products were favored.

Another fused iron catalyst was developed for the synthesis of large olefin-containing hydrocarbon fractions in the ammonia laboratory at Oppau, headed by Scheuermann.[70] This catalyst was prepared in the manner described above by fusion of iron plus promoters in a stream of oxygen.

The early tests in this project included the study of promoters such as the difficultly reducible oxides of aluminum, magnesium, calcium, and beryllium, and the easily reducible oxides of copper, silver, nickel, and cobalt. The use of aluminum oxide was abandoned because it was found to produce smaller specific yields and smaller straight-chain hydrocarbon fractions than magnesium oxide. Catalysts containing chiefly magnesium oxide, silica, and potassium as promoters were selected for further study. A rapid increase in the olefin content of the primary product from 20 per cent to 70 per cent occurred when a small quantity of alkali was introduced into the catalyst, as shown in Table 76, I. It is noteworthy that the $MgO:K_2O$ ratio was important. If the magnesia content was increased with the alkali content so that their ratio remained the same, no significant change in product was observed. Substitution of the potassium by silica, an acidic compound, caused a decrease and then a small increase in olefin content of the primary product (Table 76, II); the same effect was observed when the alkali content was constant and the SiO_2 content was increased. In the presence of a constant amount of silica, the strong effect of increasing amounts of potassium oxide (Table 76, III) on olefin content and higher-molecular-weight fractions (>320°C) was nullified. After use in synthesis, the alkalized catalysts showed, upon examination by x-ray analysis, the presence of Hägg carbide, Fe_2C. The silica-containing catalysts contained mainly magnetite (Fe_3O_4) and some Hägg carbide. In the presence of a constant quantity of silica and increasing alkali, mainly Hägg carbide and some hexagonal carbide, Fe_2C (Halle and Herbst carbide), were observed.

The catalyst finally selected had the composition $100Fe:5MgO:3.0K_2O$. It was reduced in hydrogen at 500°C and a space velocity per hour of 2,000 for 48 hr. Catalysts whose reduction value varied between 30 and 100 produced similar results. At a space velocity per hour of synthesis gas of 200, the synthesis temperature could be lowered to 225°–245°C. The data of synthesis tests with this catalyst were reported by Scheuermann [70] to have been lost.

Of interest is the observation in the same report by Scheuermann [70] that the effect of fluoride added to the I.G. Farben. fused and pre-

TABLE 76. TESTS OF FUSED IRON CATALYSTS FOR OLEFIN PRODUCTION, I.G. FARBEN., OPPAU

Catalyst Composition, per cent	Temperature, °C	CO Conversion, per cent	Yield C_5+, g per cu m [a]	>320°C Fraction, per cent of C_5+	Straight-Chain Fraction, per cent of C_5+	Olefins, per cent of fraction				Alcohols, per cent of fraction				X-ray Analysis of Used Catalyst
						<250°C	<320°C	<450°C	>320°C	<250°C	<320°C	<450°C	>320°C	
Space velocity 480 per hr, synthesis gas contained 33 per cent CO														
I. Fe-MgO-K_2O [b]														
70.2:3.4:0	253	80	70	24	65	..	..	..	19	..	..	..	4	Hägg Fe_2C
70.4:3.5:0.31	245	83	89	62	68	..	..	..	47	..	..	..	..	Hägg Fe_2C
69.9:3.5:0.53	240	82	89	69	68	..	..	..	59	..	..	..	..	Hägg Fe_2C
69.9:3.3:0.73	252	80	74	73	74	..	..	..	66	..	..	..	29	Hägg Fe_2C
68.4:3.2:1.46	245	78	78	59	66	..	..	..	68	..	..	..	18	Hägg Fe_2C
68.0:3.3:2.29	253	75	62	50	76	..	..	..	77	..	..	..	23	Hägg Fe_2C
67.0:3.2:2.34	255	90	108	48	74	..	..	..	73	..	..	..	23	Hägg Fe_2C
63.3:3.0:6.08	283	80	77	49	62	..	..	..	79	..	..	..	10	Hägg Fe_2C
II. Fe-MgO-SiO_2														
70.2:3.4:0	253	80	70	24	65	..	..	..	19	..	..	..	4	Fe_3O_4, some Hägg Fe_2C
69.8:3.3:0.85	268	70	41	13	66	..	..	..	7	..	..	..	3	Fe_3O_4, some Hägg Fe_2C
69.5:3.4:1.63	277	73	52	12	70	..	..	..	27	..	..	.	1	Fe_3O_4, some Hägg Fe_2C
68.2:3.3:3.15	263	78	55	39	78	..	..	..	36	.	..	..	5	Fe_3O_4, some Hägg Fe_2C
Space velocity 240 per hr, CO content of synthesis gas 50 per cent														
III. Fe-MgO-K_2O-SiO_2														
70.5:2.6:0:0	230	48	87	29	..	67	52	34	..	10	4	2	..	Fe, Fe_3O_4
70.7:3.1:0:1.76	230	33	58	25	..	53	41	28	..	7	3	5	..	Fe_3O_4, Fe_3C, Hägg Fe_2C
69.0:2.7:0.18:1.80	230	61	93	41	..	65	50	34	..	23	13	5	..	Hägg Fe_2C, little Fe_3O_4
68.2:3.3:0.60:1.86	230	77	118	38	..	70	55	40	..	22	9	5	..	Hägg Fe_2C, trace Fe_3O_4
68.0:3.2:1.54:1.94	230	72	122	47	..	65	55	43	..	29	24	12	..	Hexagonal Fe_2C, some Hägg Fe_2C

[a] Basis for calculation of yield was not given.
[b] Bulk density of catalysts in this group varied from 2.94 to 2.38 with increasing alkali content.

cipitated catalysts was to produce lower-boiling products at low synthesis temperatures. Catalysts containing AlF_3 or FeF_3 could be operated at temperatures as low as 170°–200°C and still produce low-boiling oils, according to Scheuermann. At these low temperatures, the oxygen was found in water rather than carbon dioxide.

A highly active fused catalyst was prepared, according to Michael,[29,70] from powdered iron oxide (Eisenrot), obtained by burning iron carbonyl vapor in oxygen. The oxide was stirred into a paste with 1 per cent of potassium carbonate or potassium borate (or sodium borate) and shaped into small cubes (about 1 cm^3), which were dried and reduced at a high space velocity of hydrogen at 350°–450°C until two-thirds of the iron was in metallic state. The reduced catalyst, protected by an atmosphere of CO_2, was mixed with the cooling oil and ground in a ball mill to a small particle size.

This catalyst was used in the foam process, in which water gas was forced through a ceramic plate at the base of a cylindrical vessel containing a suspension of catalyst in a high-boiling fraction of synthetic oil and which resulted in the production of highly olefinic liquid hydrocarbon fractions for use in chemical synthesis.[39,139] Synthesis on a pilot-plant scale was carried out at 20 atm pressure of synthesis gas and an initial temperature of 250°C in a simple tube of 1.5-cu-m capacity. The oil contained 150–300 kg iron per cu m of oil, and to it was added the necessary amounts of alkali in the form of alcoholic KOH. The slurry was recirculated at such a rate as to change the contents of the reactor every 3 min; a temperature rise of 10°C occurred in the reactor. The synthesis gas ($1CO + 1H_2$ or $1CO + 1.25H_2$) recirculation ratio was 1. Conversion of $CO + H_2$ (U) was 70 per cent in one stage and produced 350–450 g products per l of catalyst per day; 10 per cent of this yield was methane. The yield of C_3+ hydrocarbon products per cubic meter of gas converted was 189 g, distributed as follows:

Fraction	Weight Per Cent	Olefins, volume per cent
$C_3 + C_4$	10	75–80
Gasoline (C_5–200°C)	30–40	70
Middle oil (200°–325°C)	25–35	50–60
Paraffin (>325°C)	20–30 [a]	.....

[a] 67 per cent boiled over 450°C.

In addition, about 10 g of $C_1 + C_2$ hydrocarbons and 9 g of alcohols per cu m of gas converted were obtained. The gasoline fraction boiling be-

[139] W. A. Horne and W. F. Faragher, *U. S. Bur. Mines Inform. Circ.* 7,376 (1946), 27 pp; PB 7,745; *F.I.A.T. Final Rept.* 426 (1945).

low 100°C contained about 5 per cent of alcohols; the middle-oil fraction, 8–12 per cent of alcohols and in addition a similar quantity of oxygenated compounds consisting of esters, acids, aldehydes, and ketones. Additional details on this process are given in Chapter 4, p 416.

Fused, alkalized iron catalysts prepared from finely divided iron or iron oxide are described as suitable for the fluidized process in several American patents.[140–142]

Sintered Iron Catalysts

In the fixed-bed, hot-gas-recycle process, the development of which is described in Chapter 4, p 396, a hard catalyst granule was used at a temperature of 325°C and a pressure of 20 atm of $1CO + 1H_2$ gas.[29, 39, 70, 139] The catalyst was prepared as follows: Finely divided iron powder, prepared by thermal decomposition of iron carbonyl and consisting of particles 2–5 microns in diameter, was pasted with a concentrated solution of sodium borate (1 per cent borax, based on iron) and formed into small cubes of about 1 cm^3. In order to insure loose packing, the cubes were made with slightly irregular edges. They were sintered in an electrically heated furnace in an atmosphere of hydrogen at 850°C for 4 hr. True density of the catalyst was 7, and the apparent or bulk density 2.5. The catalyst was then cooled in hydrogen, which was replaced by carbon dioxide for protection during transfer to the reactor. Similar reduction of a precipitated catalyst to which 5 per cent of aluminum hydroxide had been added was also described.[143, 144]

A U. S. Bureau of Mines sintered catalyst consisted of glomerules impregnated with alkali. Glomerules were prepared by compacting a wet iron oxide powder with a high-frequency vibrator, rolling the material into rough spheres, and sintering at 1,200°C. These rough spheres were impregnated with alkali. One such catalyst was alkalized with K_2CO_3 so that its calculated composition was $100Fe:0.6K_2O$. It was reduced by hydrogen at 396°C and a space velocity of 1,000 for 43 hr and then inducted at 7 atm of $1H_2 + 1CO$ gas during a period in which the temperature was raised 7°C per hr until the CO_2-free contraction

[140] J. K. Roberts (to Standard Oil Co., Chicago), U. S. Patent 2,461,570, Feb. 15, 1949.

[141] A. Voorhies, Jr. (to Standard Oil Development Co.), U. S. Patent 2,469,755, May 10, 1949.

[142] M. A. Mosesman (to Standard Oil Development Co.), U. S. Patent 2,465,314, Mar. 22, 1949.

[143] W. Michael (to I.G. Farben.), U. S. Patent 2,183,146, Dec. 12, 1939.

[144] W. Michael and W. Jaeckle (to I.G. Farben.), U. S. Patent 2,183,145, Dec. 12, 1939.

was 63 per cent. In a 10-week continuous test the average temperature was 220.1°C, space velocity 100, contraction 64.1 per cent. The average yield of hydrocarbons, in grams per cubic meter of feed gas, was as follows: 7.6 CH_4, 27.1 C_1–C_4, 99.1 C_5+.[124]

Cemented Iron Catalysts

This type of catalyst is usually described as "sintered," but in the patent literature the term "sintered" usually refers to catalysts in which the active component has been drastically modified by heat. In "cemented" catalysts, the particles of iron oxide are held together by a binding agent. Changes that occur in the structure of the iron oxide are slight and in general are unimportant to the usefulness of the catalyst.

In U. S. Bureau of Mines catalysts, alumina and borax were suitable binding agents; potassium borate, potassium and sodium silicates, magnesia, and calcium oxide were unsuitable. The two last-mentioned materials produced active catalysts, but the granules were soft. Test data for catalysts containing the other binding agents are summarized in Table 77.[124] The first catalyst shown, A3218.087, was described pre-

Table 77. Activity of Some Cemented Magnetite Ore Catalysts in Tests at 7 Atm of $1H_2 + 1CO$ Gas

(6–10 mesh granules, reduced in H_2 for 20 hr, 450°C, SVH = 1,500–2,000, inducted and operated at 7 atm.)

Catalyst		Test, X . . .	Time, weeks	Temperature, °C	SVH	Contraction, per cent	Hydrocarbon Products, g per cu m feed gas		
No.	Composition						CH_4	C_1 C_4	C_5+
A3218.087	$100Fe:3.5Al_2O_3:0.5K_2O$	196	8	228.5	101.5	64.3	6.9	20.2	66.6
L1002.2	$100Fe_3O_4:5Na_2B_4O_7$	165	8	248.5	96.8	65.6	15.4	44.2	62.5
L1004	$100Fe_3O_4:4K_2B_4O_7$	175	2	283.0	106	58.6	20.2	41.0	53.7
A3310 [a]	$Fe_3O_4:K_2SiO_3$ [b]	146	1	297.0	98.1	60.9	26.0	58.6	35.7
L1010.2	$100Fe_3O_4:2Na_2SiO_3$	185	5	262	. . .	64.4	16.1	50.7	65.5
L1016	$100Fe_3O_4:10Na_2SiO_3$	187	2	285.0	90.0	59.4	33.8	60.9	37.1

[a] Reduction time was 39 hr.

[b] Composition based on starting materials was $100Fe:3.3SiO_2:5.5K_2O$.

viously in this chapter (p 234). Catalyst L1002.2 was prepared by mixing finely divided magnetite ore with 5 per cent borax ($Na_2B_4O_7$) solu-

tion, evaporating to dryness, and heating at 800°C for 15 min. Heating at lower temperatures produced soft granules which disintegrated in water. These two catalysts were fairly satisfactory with respect to activity and mechanical strength; however, the granules were softer in the reduced than in the oxide state. A similar preparation with potassium borate (catalyst L1004) was neither particularly active nor stable mechanically. When the binding agent was a silicate, the preparation procedure was similar. These catalysts were unsatisfactory with respect to one or the other or both criteria. Typical of the silicate-containing catalysts was A3310, which was prepared as follows: Equimolar quantities of K_2CO_3 and SiO_2 were fused; the product was a white, crystalline solid, soluble in water. An aqueous solution of this material, containing per cc 0.249 g K_2O and 0.149 g SiO_2, was mixed with finely divided magnetite ore in the proportions of 160 cc:1,000 g. The paste thus obtained was evaporated to dryness and dried in an oven at 150°C for 24 hr. The dried cake was crushed to 6–8 mesh granules, which were heated at 500°C for 16 hr.

Michael [39, 70, 139] described some highly active cemented catalysts designed for use at low temperatures in the conventional, tubular reactors operated at 20 atm. One such catalyst was prepared by mixing iron oxide or iron hydroxide with 5–25 per cent of MgO or $MgCO_3$ and 1–2 per cent of K_2CO_3 or $K_2B_4O_7$ and compressing the mixture into pellets. Heating of the pellets was done in nitrogen at 850°C. After cooling, the catalyst was reduced with hydrogen at a high space velocity and temperature of 350°–450°C. The results obtained in a test carried out at 230°–250°C in a reactor of 20-l capacity showed that the major fractions of the product comprised gasoline and middle oil; *ie*, 10 weight per cent of $C_3 + C_4$, 35–50 gasoline (<200°C), 25–35 middle oil (200°C–325°C), 15 paraffin (>325°C).

The product distribution was shifted toward high wax yields when the promoter was wolfram oxide or barium oxide.[70] For example, iron powder obtained by thermal decomposition of iron carbonyl was mixed with several per cent tungsten oxide and pasted with 1 per cent potassium borate dissolved in a little water. The mixture was formed into pellets which were heated in air at 850°C for 4 hr and then reduced in hydrogen passed at a high space velocity and a temperature of 450°C. At a synthesis temperature of 230°C the following product distribution was observed, in per cent:

$C_3 + C_4$	4
Gasoline (<200°C)	17
Middle oil (200°–350°C)	19
Paraffin (>350°C)	60

U. S. Bureau of Mines Studies of Various Sources of Iron

The results of tests with catalysts prepared from iron obtained from various sources are summarized in Table 78.[124] The catalysts were made by impregnating the iron with about 0.5 per cent of K_2O. In catalysts A3210 and L3009, alumina was incorporated as the binding agent. The catalysts prepared from pigment-grade Fe_2O_3, mill scale, goethite ore, and Pennsylvania Salt Manufacturing Company siderite were operated at temperatures below about 235°C. These catalysts were similar to the cemented catalysts prepared from finely divided magnetite ore (see p 234, this chapter) and showed nearly constant activity throughout the test, in contrast to the steady decrease in activity observed with the fused synthetic-ammonia-type catalysts. The catalyst prepared from Alabama ore was slightly less active and was equal in activity to a fused synthetic-ammonia catalyst. The low activity of the catalysts prepared from wrought iron drippings and limonite ore could probably be attributed to the presence of some deactivating constituent in the raw material. The former catalyst contained a large amount of silica (30 per cent in the raw material) and was difficult to reduce; the latter catalyst was probably inactive because of its high sulfur content (total sulfur was 1.2 per cent). The conclusion that may be drawn from these tests is that an inexpensive iron powder may be used to prepare active catalysts, provided (1) that it does not contain a constituent which is a catalyst poison in the Fischer-Tropsch synthesis or which hinders reduction of the catalyst, and (2) that it is impregnated with alkali.

Present Status

U. S. Bureau of Mines studies have produced several promising catalysts. Three which were developed as a result of the tests described in the preceding pages were the following: (1) magnetite or other iron oxide powder cemented with Al_2O_3 and alkalized with K_2O; (2) glomerules prepared by compacting a wet iron oxide powder with a high-frequency vibrator, rolling the material into rough spheres, sintering at 1,200°C, and impregnating the spheres with alkali; (3) magnetite or other iron oxide powder cemented with 5–10 per cent of borax. These catalysts were rather completely reduced in 20 hr at 450°C. Catalysts of types 1 and 2 were active at operating temperatures of 235°C or lower, and those of type 3 were somewhat less active, operating at about 250°C.

The life of two catalysts consisting of cemented magnetite-borax glomerules was 40–50 days. In preparing these catalysts, a dry mixture was made of finely divided magnetite and borax. Sufficient water (about

TABLE 78. U. S. BUREAU OF MINES TESTS OF IRON CATALYSTS PREPARED FROM VARIOUS RAW MATERIALS, AT 7 ATM OF $1H_2 + 1CO$ GAS

(6–8 mesh granules; reduced in H_2, 38 hr, 450°C, SVH = 2,500; inducted at 7 atm of $1H_2 + 1CO$, temperature raised 7° per hr until contraction was 63 per cent.)

Catalyst			Synthesis Data										
								Products, g per cu m feed gas					
No.	Source of Iron	Composition	Test, X . . .	Time, weeks	Temperature, °C	Contraction, per cent	Space Velocity	CH_4	$C_3 + C_4$	C_1–C_4	C_5+	CO_2
A3210	Pigment grade, Fe_2O_3	$100Fe:4.5Al_2O_3:0.96K_2O$	134	3	236.3	65.5	99.7	15.3	29.0	57.8	64.8	351.0
L3009 [a]	Mill scale	$100Fe:3.5Al_2O_3:0.6K_2O$	156	5	237.2	65.0	100.4	13.5	16.7	37.1	65.4	301.1
A2103 [b]	Goethite ore, α-$Fe_2O_3 \cdot H_2O$	$100Fe:0.5K_2O$	181	4	230.5	65.5	100	8.5	17.5	34.0	68.3	238.4
L2014 [c]	Pa. Salt Co. siderite, $FeCO_3$	$100Fe:0.5K_2O$	233	4	232.0	65.7	98	5.3	11.4	21.5	72.2	331.9
L2013 [a, c]	Alabama ore	$100Fe:0.5K_2O$	232	3	256.0	66.5	99	12.7	22.2	42.8	83.7	284.3
A3312 [d]	Wrought iron drippings	$100Fe:62SiO_2:1K_2O$	177	2	300.0	27.1	100	5.5	4.7	14.1	12.7	143.4
A2104 [a, b]	Limonite ore	$100Fe:3SiO_2:1.6Al_2O_3:0.8K_2O$	202	1	294	9.3	93	2.0	0.4	4.8	0.2	20.8

[a] Reduction space velocity 1,500.
[b] Reduction time 24 hr.
[c] Reduction temperature 400°C.
[d] Reduction space velocity 4,000.

15 per cent by weight) was added to produce a heavy paste, which was extruded through a vibrating perforated plate into a rotating drum. Spherical glomerules were thus produced, which were heated at 1,000°C for about 15 min. Catalyst L1017 contained 7.5 per cent borax, and L1006.11, 10 per cent. Catalyst 1017, in test X199, maintained a relatively constant activity at about 255°C for 40 days. After 40 days, it became necessary to increase the temperature steadily, whereupon the activity became constant again at 285°–295°C in the operating period from 60 to 80 days. After 50 days of testing, the catalyst was removed for examination. It dropped freely from the reactor, and the particles had, apparently, not changed in size or in mechanical strength during this period. The catalyst was recharged into the reactor, and the test continued to about 80 days. When the run was terminated, the catalyst was found to be caked in the reactor, although no excessive pressure drop through the catalyst bed was observed.

A similar catalyst, L1006.11, containing slightly more borax, produced similar results in test X205. The temperature required to maintain constant conversion varied between 255°C and 260°C for 45 days, but subsequently it was necessary to increase the temperature to 300°C in the next 7 days. The test was terminated after several days at 300°C, and the catalyst was found to be badly disintegrated, presumably as a result of operation at this high temperature. Possibly, if catalysts of this type were hydrogenated at 400°or 450° C when increase in temperature became necessary, the catalyst life could be extended appreciably. However, the present data indicate a life of 45–50 days for these catalysts. A summary of the data obtained in tests X199 and X205 is shown in Table 79.[124]

It should be noted that the U. S. Bureau of Mines tests described in the preceding pages were made in fixed-bed, externally cooled, laboratory-size reactors. The suitability of catalysts on a large scale or in other types of reactors, with respect to rigidity of the catalyst granules, would have to be determined. For example, the borax and alumina cemented catalysts retained some of their mechanical strength upon reduction, but the glomerule catalysts lost their mechanical stability and would be unsuitable in a process requiring a rigid granule. The latter type of catalyst would probably be satisfactory in the slurry process. Recently, ball clay has shown some promise of being a successful cementing agent.

The use of nitrided fused iron catalysts, prepared by the introduction of nitrogen into the iron lattice, has resulted in a marked increase in catalyst activity and life. These catalysts represent a significant advance in the search for a theoretical basis for catalyst development. A detailed description of them is presented in Chapter 6, p 549.

TABLE 79. LIFE TESTS OF CEMENTED MAGNETITE-BORAX GLOMERULES AT 7 ATM OF $1H_2 + 1CO$ GAS

(6–10 mesh granules; reduction conditions: H_2, 20 hr, 450°C, space velocity 2,000; induction conditions: 7 atm of $1H_2 + 1CO$ gas, temperature raised 7°C per hr until contraction was 63 per cent.)

Period, hr	Temperature, °C	Contraction, per cent	Space Velocity	Products, g per cu m of feed gas						$\frac{C_5+}{C_1-C_4}$	C_5+, per cent of total hydrocarbons
				CH_4	$C_3 + C_4$	C_1-C_4	CO_2	H_2O	C_5+		
Catalyst L1017, 7.5 per cent borax, test X199											
112	256	63.5	91	13.9	25.2	49.5	259.7	30.4	39.0	0.8	44.1
166	257	62.7	92	19.8	18.2	52.7	353.7	35.7	65.6	1.2	55.5
162 [a]	254	64.3	92	23.5	20.0	58.9	326.3	28.2	58.5	1.0	49.8
166	254	62.7	91	23.5	24.8	63.0	316.9	27.8	49.7	0.8	44.1
190	256	63.4	90	27.5	23.3	66.5	317.0	25.5	57.0	0.9	46.2
142	258	61.9	91	29.2	25.7	72.1	326.9	12.7	44.4	0.6	38.1
166	260	62.9	89	24.8	24.9	63.5	321.9	22.3	46.7	0.7	42.4
166 [b]	265	60.1	92	25.4	13.6	52.7	315.9	16.7	42.2	0.8	44.5
166	269	62.6	88	27.0	31.2	71.3	327.0	21.2	38.9	0.5	35.3
166	265	64.6	90	31.7	15.2	59.9	331.6	19.0	38.1	0.6	38.9
166	292	68.1	88	32.9	25.1	70.2	339.5	21.1	42.8	0.6	37.9
166	288	66.6	90	33.9	23.3	69.1	346.1	18.3	39.1	0.6	36.1
166	287	64.5	89	38.0	20.4	68.8	355.9	13.5	44.4	0.6	39.2
Av. 166	258	62.6	93	24.8	21.5	66.1	325.5	24.1	52.0	0.9	45.8
Catalyst L1006.11, 10 per cent borax, test X205											
88	267	63.6	101	27.5	23.9	68.4	279.2	35.6	38.1	0.6	35.7
166	258	65.6	101	19.9	24.5	57.4	303.5	29.8	54.8	0.9	48.9
166	256	63.8	101	10.3	43.0	61.2	312.9	35.3	52.1	0.8	46.0
166	256	61.3	102	23.2	27.8	63.1	293.4	29.6	42.6	0.7	40.3
166	256	64.1	100	24.9	9.7	48.1	295.0	32.6	41.0	0.8	46.1
166	260	64.3	103	24.4	27.8	64.3	294.3	28.1	46.2	0.7	41.8
126	263	64.1	101	27.1	23.6	65.9	302.4	20.5	44.1	0.7	40.1
166	268	61.0	102	26.7	30.0	71.1	309.2	21.2	34.7	0.5	32.8
165	290	64.4	101	33.3	21.8	69.5	341.4	15.7	35.3	0.5	33.2
Av. 160	260	63.5	101	22.4	26.6	61.6	301.5	28.2	45.1	0.7	40.5

[a] Power off 4 hr.

[b] Two-cubic-centimeter sample removed at the end of this period. At this point, catalyst granules were in good condition.

PARTICLE SIZE

U. S. Bureau of Mines tests of samples of a fused iron catalyst of different particle sizes showed that the activity of this catalyst increased with decreasing particle size until a mesh size of 40–60 was reached, after which the activity remained approximately constant. This in-

formation is of practical importance, since the catalyst may then be operated to produce a higher space-time-yield (yield per unit volume of catalyst per unit time) at the same temperature, or the same space-time-yield at a lower temperature, which is more favorable to a lower production of gaseous hydrocarbons and a longer catalyst life.

Activity and product-distribution data obtained in tests of various samples of synthetic-ammonia-type catalyst D3001 are summarized in Table 80.[124] The temperature required to maintain a gas contraction of

Table 80. Activity and Product-Distribution Data of Various Particle Sizes of Fused Catalyst D3001

(All catalysts reduced in hydrogen at 450°C and tested at 7 atm of $1H_2 + 1CO$ gas.)

	Test, X . . .							
	212		152		118		201	
Mesh size	4–6		6–8		14–18		40–60	
Geometric area, sq cm per g [a]	4.0		5.2		11.9		44.7	
Space velocity	97.6		97.0		98.9		99.0	
Contraction, per cent	63.1		65.2		62.3		64.8	
Average synthesis temperature, °C	266		256		238		220	
Equivalent activity at 238°C [b]	14.1		19.9		37.5		73.2	
Products, weight per cent [c]								
C_1	17.8		17.8		10.7		7.1	
C_2	9.1		9.5		7.4		5.8	
$C_3 + C_4$	17.1		19.9		15.2		14.0	
Liquids plus solids	56.0		52.8		66.7		73.1	
Total acid number [d]	1.33		1.98		5.67		3.62	
Distillation analysis of C_5+, weight per cent								
<185°C	48.7		38.1		27.8		19.8	
185°–352°C	34.2		35.5		34.9		24.3	
352°–464°C	10.3		14.9		16.9		15.9	
>464°C	6.8		11.5		20.4		40.0	
Infrared analysis of fractions [e]	<185°	185–352°	<185°	185–352°	<185°	185–352°	<185°	185–352°
OH	0.15	0.04	0.17	0.04	0.48	0.10	2.10	0.70
α-Olefins	4.16	1.10	4.87	1.10	5.40	1.29	7.40	3.40
β-Olefins	5.60	3.66	5.05	3.88	3.46	3.43	1.60	1.90

[a] Computed as smooth spheres or cubes.

[b] Cubic centimeters $1H_2 + 1CO$ gas converted per gram of catalyst per hour. An activation energy of 20 kcal per mole was used in calculation at 238°C.

[c] Total of C_1–C_4 and liquids plus solids, per cubic meter of feed gas, varied from 100–110 g.

[d] Average acid number of aqueous plus hydrocarbon phases.

[e] Weight per cent of actual group, *i.e.*, OH or C=C.

63–65 per cent (CO_2-free) decreased with decreasing particle size; the equivalent activity at 238°C increased. Thus, activity of a fused catalyst apparently varied inversely with the particle diameter: accessibility of the catalyst surface appears to be an important factor in the Fischer-Tropsch synthesis.

PRETREATMENT AND REACTIVATION OF IRON CATALYSTS

Pretreatment Conditions

The Kaiser Wilhelm Institut für Kohlenforschung reported that the procedure developed for conditioning cobalt catalysts, *ie*, reduction of the catalyst by hydrogen before synthesis, was unsuccessful when applied to precipitated iron catalysts in the medium-pressure synthesis. From 1937 on, KWI research on the Fischer-Tropsch synthesis was concerned primarily with the development of procedures for activating precipitated alkalized iron catalysts. In 1940, Pichler [102] reported the results of pretreatment studies with CO and CO-H_2 mixtures. In Table 81 are presented activity data for catalysts pretreated under various conditions and tested in synthesis at 15 atm of $3CO + 2H_2$ and a throughput of 4 l per 10 g Fe per hr. Pretreatment under synthesis conditions, assuming the first few days of synthesis to be the conditioning (or induction) period, activated the catalyst very slowly. The effect of this induction procedure is demonstrated in the first experiment in Table 81 (column *A*), in which 4 l of $3CO + 2H_2$ gas per 10 g of iron per hr at 245°C and 15 atm pressure was passed over a sample of KWI "normal" iron catalyst (described in this chapter, p 248). The catalyst was tested in a 12–13-mm-I.D. tube which was slightly inclined from the horizontal and which was heated in an aluminum-block furnace. A layer of catalyst 30 cm long was used; it contained the equivalent of 10 g of iron, corresponding to about 20 cc of freshly prepared catalyst. At the end of the fourth day, the contraction was 10 per cent; this was the induction period. In the second and third months at temperatures above 280°C, contractions of about 45 per cent (includes CO_2) were observed. At the end of the third month, the yield per cu m of $3CO + 2H_2$ gas was 3 g of paraffin, 93 g of liquid hydrocarbons, and 32 g of gasol ($C_3 + C_4$) hydrocarbons, obtained at 280°C. In the second experiment of Table 81 (column *B*), an ammonia-precipitated iron catalyst containing 0.25 per cent of potassium carbonate was inducted with $1CO + 2H_2$ gas at atmospheric pressure and 245°C. At the end of 5 days, when the contraction was 31 per cent, the pressure was increased to 15 atm and the gas composition changed to $3CO + 2H_2$, for the synthesis period. The catalyst produced a contraction of about 59 per cent at once and continued to give high contractions for more than 3 months. The maximum temperature was 265°C, which was 38°C below the maximum synthesis temperature required in the previous experiment. In the preparation of the catalyst used in this test, ammonia was passed into a warm

(60°C) ferric nitrate solution (100 g Fe per l) at a rate calculated to complete the precipitation in 20 min. An equal volume of boiling distilled water was added to the precipitate, and it was then filtered and washed 5 times with hot distilled water. Subsequent treatment was performed in the manner described for the normal iron catalyst. The dried cake was also dark brown and hard, and it gave a conchoidal fracture.

When an iron catalyst was inducted for 25 hr at 325°C and 0.1 atm of $3CO + 2H_2$ gas, a low synthesis temperature at 15 atm of $3CO + 2H_2$ gas was maintained for a long time, as shown in the test data summarized in column *C* of Table 81. The synthesis temperature did not exceed 250°C in 100 days or 275°C in 200 days. At the end of the second week, the yield of liquid and solid hydrocarbons, per cu m of $3CO + 2H_2$ gas, was 109 g, and the yield of gasol hydrocarbons, 31 g.

These experiments showed that induction at elevated pressures was undesirable but that atmospheric- or subatmospheric-pressure induction produced active catalysts. Low induction pressure favored low free-carbon and high carbidic carbon content in the catalyst. The same trend was observed when pure CO, instead of $CO-H_2$ mixtures, was used: the catalyst inducted at 15 atm was less active than others inducted at 1 and 0.1 atm, respectively. More free carbon was deposited on the catalyst, under comparable conditions, when CO rather than $CO-H_2$ mixtures was used for induction.

That the induction temperature had an important effect upon the temperature at which synthesis could be started was indicated by the results summarized in Figure 42. In this study, samples of normal iron catalyst were inducted at 0.1 atm of $3CO + 2H_2$ gas for 25 hr at temperatures ranging from 255° to 355°C and were tested with $3CO + 2H_2$ gas at 15 atm and a throughput of 4 l per 10 g Fe per hr. Synthesis temperature was kept constant at 235°C and the decrease in contraction with time was measured. The optimum temperature range was observed to be 315°–325°C. Induction at 315°C produced a catalyst which at 235°C maintained contractions over 50 per cent (includes CO_2) for more than 30 days; induction at 325°C produced higher initial activity which declined somewhat more quickly. Other tests showed that catalysts inducted at 245° and 235°C, respectively, and 1 atm of $CO-H_2$ gas could not reach a contraction of 50 per cent at a synthesis temperature of 235°C and synthesis pressure of 15 atm. Analysis of such catalysts showed that there was a sharp increase in carbidic carbon between 250° and 450°C, with a maximum at 325°C. Free carbon showed a sharp increase at temperatures above 325°C.

TABLE 81. EFFECT OF INDUCTION PRESSURE AND TEMPERATURE UPON ACTIVITY OF IRON PRECIPITATED CATALYSTS IN MEDIUM-PRESSURE SYNTHESIS

(Synthesis conditions: $3CO + 2H_2$, 15 atm, 4 l per 10 g Fe per hr.)

Catalyst [a]	*A*			*B*			*C*			*D*			*E*		
Time, days	Temperature, °C	Contraction, per cent	C_5+, g per cu m [b]	Temperature, °C	Contraction, per cent	C_5+, g per cu m [b]	Temperature, °C	Contraction, per cent	C_5+, g per cu m [b]	Temperature, °C	Contraction, per cent	C_5+, g per eu m [b]	Temperature, °C	Contraction, per cent	C_5+, g per cu m [b]
1	245	4	..	245	59	..	235	56	...	235	47	...	235	55	...
2	...	..	..	245	48	..	...	..	...	235	50	...	...	..	...
4	245	10	..	250	53	..	...	..	...	...	..	...	...	..	...
5	250	13	..	250	49	..	235	56	...	235	50	...	235	50	...
7	253	17	..	...	..	..	...	..	...	...	..	...	...	..	...
10	...	..	..	252	46	..	235	56	...	235	51	...	235	51	...
11	260	24	..	...	..	..	...	..	...	...	..	...	...	..	...
13	270	24	..	...	..	..	...	..	...	...	..	...	...	..	...
14	275	37	..	...	..	..	...	..	109	...	..	...	...	..	...
20	...	..	..	256	51	..	235	52	...	235	55	...	235	51	...
28	280	36	..	...	..	..	...	..	...	...	..	...	...	..	...
30	...	..	..	...	..	..	237	48	...	...	..	...	...	..	...
40	...	..	..	...	..	..	240	52	...	...	..	108	235	53	...
50	...	..	..	255	51	..	240	50	...	235	54	...	...	..	110
60	290	50	..	...	..	..	241	48	...	...	..	...	235	53	...

69	268	37	..	...	..	..	...	..	...	...	..	...	...	..	...
70	...	..	..	...	..	..	247	53	...	...	..	105	...	..	...
75	280	47	..	...	..	..	...	..	...	...	..	...	...	..	...
80	...	..	..	...	..	..	250	54	...	...	..	...	235	49	...
90	280	49	96	...	..	..	249	53	...	...	..	...	...	..	...
98	283	44	..	...	..	..	...	..	...	...	..	...	...	..	...
100	...	..	..	265	55	..	252	52	...	235	53	110	248	54	...
106	285	43	..	...	..	..	...	..	...	...	..	...	...	..	...
110	...	..	..	...	..	..	248	48	...	...	..	...	...	..	...
120	...	..	..	...	..	..	256	48	...	...	..	...	250	49	...
130	288	43	..	...	..	..	264	56	...	235	47	...	...	..	...
140	292	44	..	...	..	..	269	47	...	245	48	...	...	..	...
150	298	47	..	...	..	..	270	43	...	...	..	...	...	..	...
160	...	..	..	...	..	..	270	47	...	250	49	...	...	..	...
170	...	..	..	...	..	..	277	44	...	...	..	...	...	..	...
180	...	..	..	...	..	..	278	43	...	251	50	...	...	..	...
190	...	..	..	...	..	..	272	46	...	...	..	...	...	..	...
200	...	..	..	...	..	..	273	47	...	250	44	...	...	..	...
250	...	..	..	...	..	..	...	..	...	265	50	...	...	..	...
300	...	..	..	...	..	..	...	..	...	263	43	110	...	..	...
350	...	..	..	...	..	..	...	..	...	270	40	...	...	..	...

[a] *A.* Induction with $3CO + 2H_2$ at 15 atm, 4 l per 10 g Fe per hr.
B. Induction, $1CO + 2H_2$, 1 atm, 245°C, for 5 days, 4 l per 10 g Fe per hr.
C. Induction, $3CO + 2H_2$, 0.1 atm, 325°C, 25 hr, 4 l per 10 g Fe per hr.
D. Induction, CO, 0.1 atm, 325°C, 25 hr, 4 l per 10 g Fe per hr.
E. Induction, CO, 0.1 atm, 345°C, 25 hr, 4 l per 10 g Fe per hr.

[b] Grams per cubic meter $3CO + 2H_2$ gas.

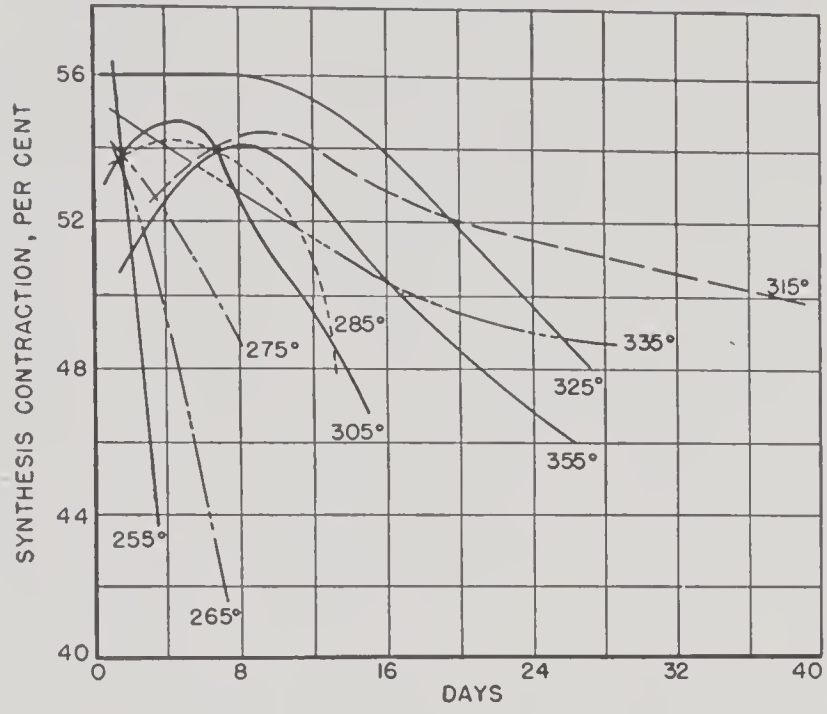


FIGURE 3–42. Influence of induction temperature upon the activity of the catalyst during medium-pressure synthesis (measured by variation of contraction with time of operation at 15 atm and 235°C). Induction was carried out for 25 hr with $3CO + 2H_2$ gas at 0.1 atm pressure. Reproduced from reference 102.

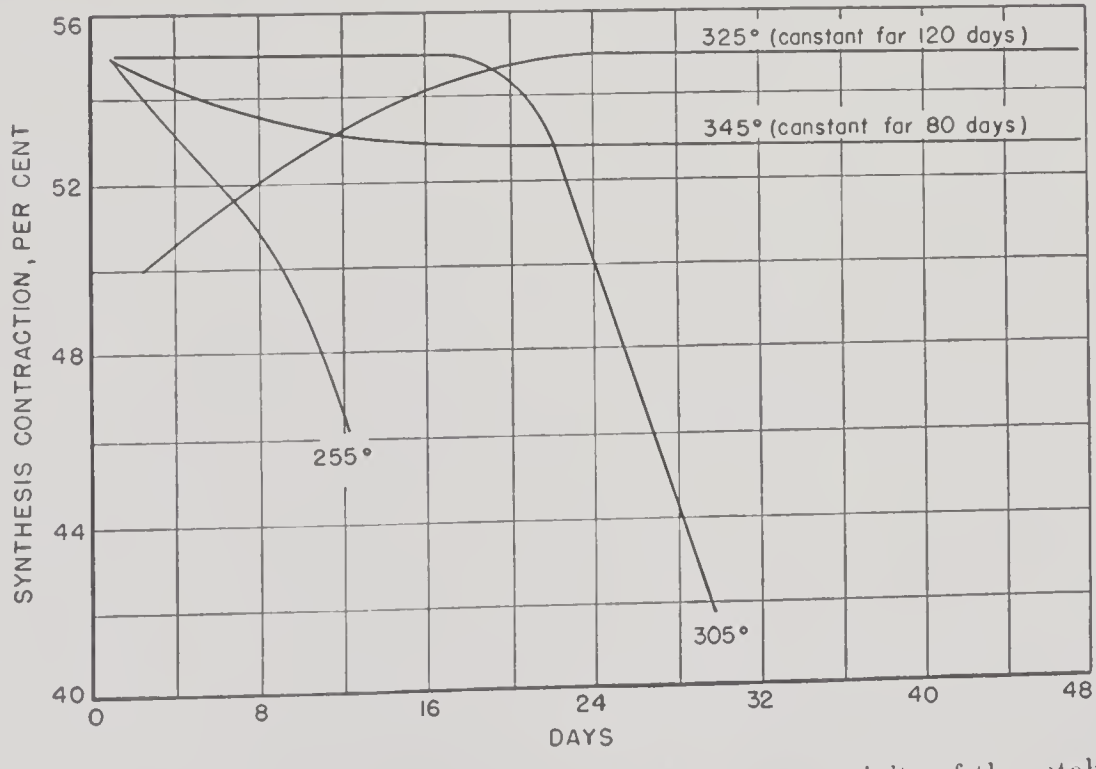


FIGURE 3–43. Influence of induction temperature upon the activity of the catalyst during medium-pressure synthesis after induction with CO at 0.1 atm pressure. Reproduced from reference 102.

The effect of induction temperature when CO was used is demonstrated in Figure 43. Induction was carried out for 25 hr at 0.1 atm of CO and a throughput of 4 l per 10 g Fe per hr, over the temperature range 255°–345°C. The synthesis conditions were 15 atm of $3CO + 2H_2$ gas, throughput of 4 l per 10 g Fe per hr, and a constant temperature of 235°C. The catalyst inducted at 325°C maintained a contraction of more than 50 per cent, at a synthesis temperature of 235°C, for 120 days; for the catalyst inducted at 345°C the contraction was higher than

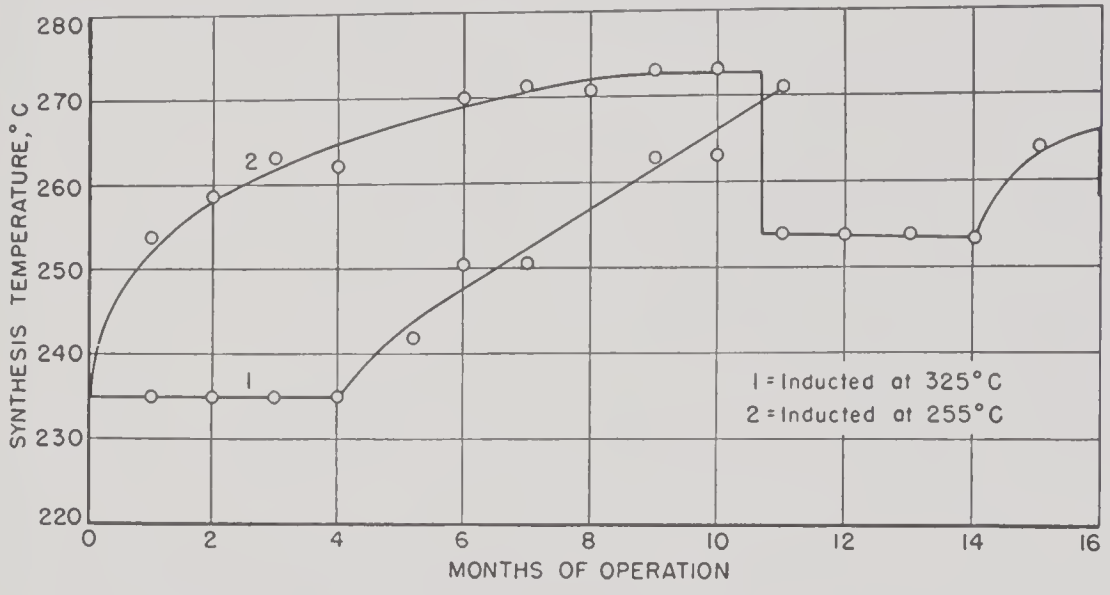


FIGURE 3–44. Influence of induction temperature upon the activity of the iron catalyst during medium-pressure synthesis. Reproduced from reference 102.

50 per cent at 235°C for more than 80 days. Synthesis test data for these two iron catalysts are shown in Table 81. In the 4-month test of the catalyst inducted at 345°C (column *E*), the average yield, per cu m of $3CO + 2H_2$ gas, for the first 2 months was 110 g C_5+ hydrocarbons and 41 g $C_3 + C_4$ hydrocarbons. In the 12-month test of the catalyst inducted at 325°C (column *D*), the average yield was 108 g C_5+ and 46 g $C_3 + C_4$ hydrocarbons. The course of this experiment is also shown graphically in Figure 44 (curve 1) in which synthesis temperature was plotted against time, in months. Curve 2 was obtained from a catalyst inducted at 255°C and 0.1 atm of CO, for 25 hr. During synthesis on the latter catalyst at 15 atm of $3CO + 2H_2$ gas and throughput of 4 l per 10 g Fe per hr, the temperature was raised from 235° to 272°C in 8 months, in order to obtain contraction values over 50 per cent (includes CO_2, equivalent to 70 per cent conversion). In the eleventh month, the increased activity permitted a lowering of the synthesis temperature to 254°C. Thereafter, the temperature was not raised again until the fourteenth month. Apparently, the catalyst inducted at this

low temperature required further conditioning, which occurred in the early period of synthesis. It was observed in this experiment, however, that a high fraction of gaseous hydrocarbons was produced and that the synthesis temperature remained above 250°C.

The effect of varying the pressure and space velocity of carbon monoxide on the rate of induction of a precipitated iron catalyst was determined by measuring the production of carbon dioxide during the

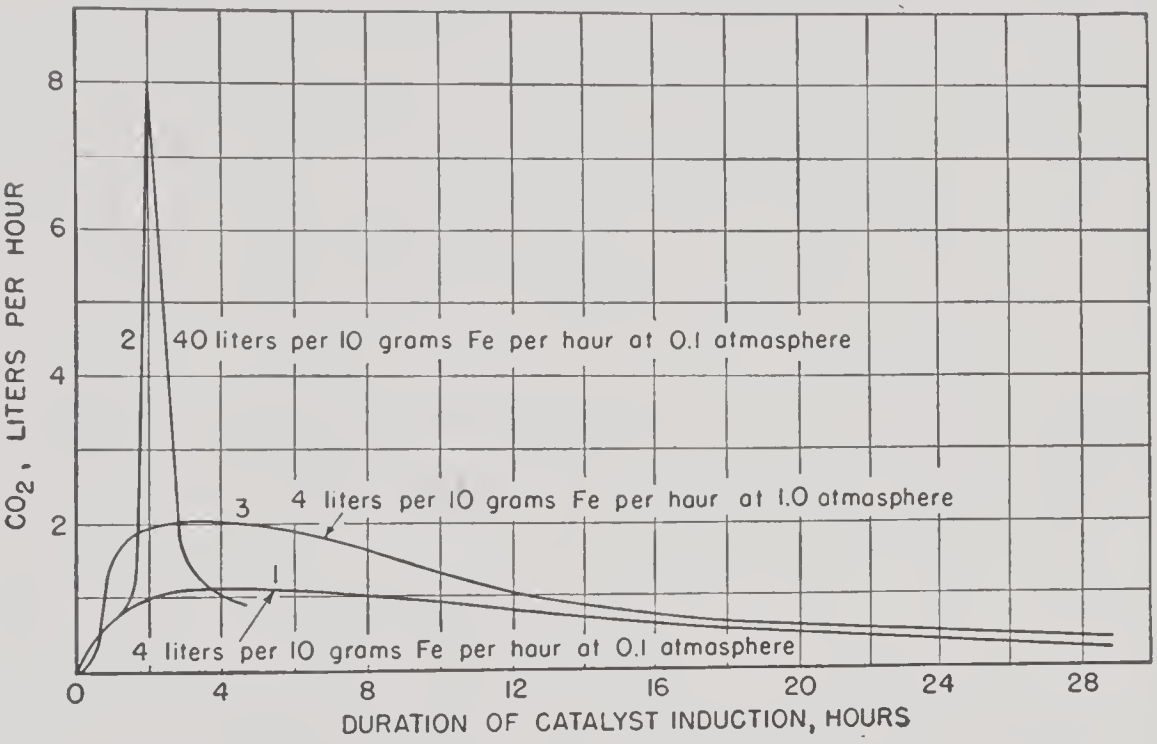


FIGURE 3–45. Rate of carbon dioxide production during induction of a precipitated iron catalyst at 325°C with different pressures and space velocities of carbon monoxide. Reproduced from reference 102.

pretreatment. Figure 45 (curves 1 and 2) shows the results obtained when induction was carried out at 0.1 atm and 325°C. A throughput of 4 l of CO per 10 g of iron per hr was used in both experiments during the preliminary period, in which the temperature was raised to 325°C. In the first experiment (curve 1), in which the throughput was 4, CO_2 production for the first 8 hr was about 1 l per hr; after this time it gradually decreased until a constant minimum value of 0.2–0.3 l per hr was reached in another 17 hr. In the second experiment (curve 2), in which the throughput was 40, a maximum value of 8 l of CO_2 per hr was reached within 2 hr and a constant minimum of 1 l per hr within the next half hour. Although in each experiment a total of 100 l of CO was passed over the catalyst until the CO_2 production decreased to a low value, more free carbon was deposited on the catalyst and more CO_2 (16 l as compared with 11 l) was produced in the first experiment than in the

second. The two catalysts showed equal activity when tested in synthesis for 30 days with $3CO + 2H_2$ gas at 15 atm and 235°C. Curve 3, obtained from another sample of catalyst inducted at 1 atm of CO and a throughput of 4, was similar to curve 1, but produced CO_2 at twice the rate in the first 8 hr.

In the Ruhrchemie laboratory, it was customary to reduce precipitated iron catalysts with hydrogen. Roelen [35] reported that reduction with hydrogen produced catalysts which favored the methane and lighter hydrocarbon fractions. Ruhrchemie found that pretreatment with water gas in place of hydrogen decreased methane production; the data summarized in Table 82 demonstrate this effect.[111] The advantages

Table 82. Effect of Pretreatment of Precipitated Iron Catalyst, 100Fe:5Cu:10CaO:30 Kieselguhr [a] (Ruhrchemie)

Test No.	Pretreatment	Synthesis Data			
		Temperature, °C	Conversion U [b]	M_v [c]	Use Ratio (X), H_2:CO
777	$1H_2 + 1CO$	214	55	12	1.1
736 [d]	$1H_2 + 1CO$	221	59	12	1.1
714	H_2	210	40	20	1.0
715	H_2	215	70	22	1.2
726	H_2	214	58	22	0.9
712	H_2	223	48	20	1.0

[a] All catalysts were precipitated by Na_2CO_3 and alkalized with potassium water glass, except the catalyst in test 777, which was alkalized with KOH.

[b] Per cent $CO + H_2$, converted.

[c] CH_4, per cent of $CO + H_2$ converted.

[d] Produced yellow paraffin.

of carrying out the pretreatment with water gas at 0.1 atm, as described by the Kaiser Wilhelm Institut für Kohlenforschung, could be reproduced by diluting the water gas with nitrogen and using a partial pressure of $CO + H_2$ of 0.1 atm at a total pressure of 1 atm.[35] Ruhrchemie (Roelen) [35] thought that pretreatment was more economical than hydrogen reduction.

A pretreatment technique described by Kölbel, of Rheinpreussen,[29,129] was the "typhoon" method. A precipitated iron catalyst was pretreated for 6 hr at 280°–320°C by $2H_2 + 1CO$ gas which was carefully

freed from both carbon dioxide and water vapor and was passed over the catalyst at atmospheric pressure and at 20 times the normal synthesis gas rate either directly or with recirculation (recirculation ratio 3). In the medium-pressure synthesis, a catalyst pretreated in this manner showed increased activity, as indicated by a low synthesis temperature and low methane production. It was believed at Lurgi that pretreatment comprised nothing more than reduction and could be done equally well with hydrogen, water gas, or diluted carbon monoxide, but hydrogen was preferred for full-scale operation for two reasons: (1) If water gas were used, the pretreatment would have to be done in the reactor itself because some synthesis would undoubtedly occur; however, the reactors could not be used at the high temperatures required for the pretreatment. (2) On account of the very high gas rate required, the water gas would have to be recirculated and would have to be scrubbed free of synthesis products before passage through the recirculation pumps.[29] Pretreatment in practice was carried out at Lurgi in the synthesis unit with hydrogen at an hourly space velocity of 1,000 for 1–3 hr at 250°–300°C, the exact time and temperature depending upon the alkali and copper content. Higher alkali contents required longer reduction periods. The catalyst containing 25 per cent copper could be reduced at 250°C; 10 per cent copper, at 280°C; and a copper-free catalyst required a temperature over 300°C.[29,39,127] If carbon monoxide-containing gas was used for pretreatment, the temperature was 180°–200°C. It was stated that, if the catalyst was intended for high wax production, it should be reduced only until 10 per cent metallic iron was present, but that if gasoline was the principal product, reduction should be carried as far as possible by increasing the time and gas rate.

In the conditioning of fused and sintered catalysts, U. S. Bureau of Mines tests showed that reduction with hydrogen was preferable to induction with $1H_2 + 1CO$ gas, but that induction at a high temperature produced satisfactory catalysts in instances in which induction rather than reduction was desirable. The data obtained in tests with sintered catalyst A2103 (goethite ore + K_2O) showed that its activity, as indicated by the synthesis temperature required to produce a contraction of about 65 per cent, increased with temperature of induction, and that the sample inducted at 325°C was nearly as active as the one reduced in hydrogen. Table 83 presents a summary of these results.[124]

The activity of fused synthetic-ammonia catalyst D3001 was increased by the presence of 0.4 per cent of CO in the hydrogen used for reduction. The average synthesis temperature for a catalyst reduced with hydrogen containing traces of CO was 248°C, which was 8°C lower than that observed in tests of the same catalyst reduced in pure hydrogen.[124]

TABLE 83. PRETREATMENT OF SINTERED CATALYST A2103, TESTED AT 7 ATM OF $1H_2 + 1CO$ GAS (U. S. BUREAU OF MINES)

Test X...	Pretreatment Conditions [a]					Synthesis Conditions			
	Gas	Temperature, °C	Time, hr	Space Velocity	Weight Loss, per cent	Weeks	Space Velocity	Temperature, °C	Contraction, per cent [b]
181	H_2	450	24	2,000	35.6	5	100	231	64.8
183	$1H_2+1CO$	270	24	100	....	5	99	270	65.1
188	$1H_2+1CO$	282	24	100	....	7	97	264	64.4
216	$1H_2+1CO$	325	24	104	....	5	100	237	63.0

[a] Pressure was atmospheric.
[b] CO_2-free.

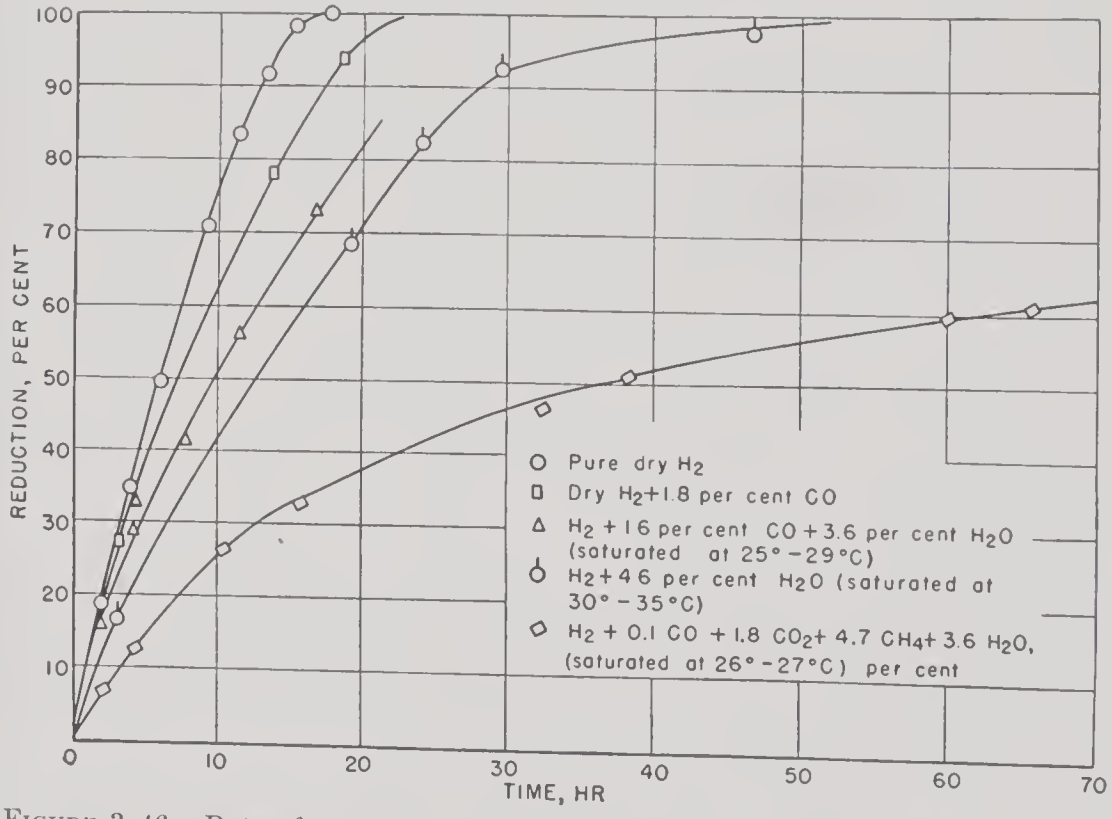


FIGURE 3–46. Rate of reduction of fused synthetic-ammonia-type catalyst D3001 at 550°C in pure dry H_2 and in H_2 containing various amounts of CO, CO_2, CH_4, and H_2O. Unpublished work of U. S. Bureau of Mines.

Other tests showed that the rate of reduction of fused synthetic-ammonia catalyst D3001 at 550°C was decreased by the presence of small amounts of carbon dioxide, water vapor, and carbon monoxide. The relative effectiveness of these three materials, in order of decreasing magnitude, was CO_2, H_2O, and CO. Reduction by a mixture of hydrogen, saturated with water vapor at 27°C, + 0.1 per cent CO + 1.8 per cent CO_2 + 4.7 per cent CH_4 was very slow at 550°C. Figure 46 [124] shows graphically the results mentioned above. It seems improbable that the methane contributed to the decreased rate of reduction.

Carbide Content

The nature of the carbide or mixture of carbides produced in iron catalyst has been studied by x-ray diffraction and thermomagnetic analyses. Table 84 is a summary tabulation, in which the carbide contents of various iron catalysts are presented. The catalysts listed are discussed in the following pages.

Table 84. Carbide Content of Iron Catalysts

Catalyst				
Composition	Type	Laboratory [a]	Pretreatment Conditions	Carbide
100Fe:0.25K_2CO_3	Precipitated	KWI	CO at 325°C	Hägg
100Fe:0.25K_2CO_3	Precipitated	KWI	H_2 at 250°C + CO at 220°C	Hägg
100Fe: (0.2–0.5)Cu: 1K_2CO_3	Precipitated	Rheinpreussen	H_2-CO, temperature not given	Hägg
Fe_3O_4-MgO-SiO_2-Cr_2O_3-K_2O	Fused	BM	H_2 at 450°C + CO at 240°C	Hägg
100Fe: 1Cu: 1.5K_2CO_3	Precipitated	KWI	CO at 325°C	Hägg + a little hexagonal
100Fe: 1Cu: 1.5K_2CO_3	Precipitated	KWI	1H_2 + 1CO at 325°C	Hägg + a little hexagonal
100Fe: 1Cu: 1.5K_2CO_3	Precipitated	KWI	H_2 at 250°C + CO at 220°C	Hägg + hexagonal
100Fe: 1Cu: 0.25K_2CO_3	Precipitated	KWI	CO at 205°C	Hexagonal
Fe: Cu: Al_2O_3: K_2O Fe: Cu: MgO: K_2O	Precipitated	IG	H_2-CO at 240°C or CO at 220°C	Hexagonal
100Fe: 10Cu: 0.32K_2CO_3	Precipitated	BM	H_2 at 220°C + CO at 240°C	Hexagonal
100Fe: 20Cu: 1.5K_2CO_3	Precipitated	KWI	2H_2 + 1CO at 225°C	Hexagonal + Hägg
Fe: Al_2O_3: K_2O	Fused synol	IG	H_2 at 450°C	Hexagonal + a little Hägg [b]

[a] Literature references are given in the text.
[b] After use in synthesis.

Quantitative determination of carbidic carbon by treatment of a completely carburized sample of KWI normal iron catalyst with hydrogen at atmospheric pressure and 263°C indicated the presence of an iron carbide containing 8.64 per cent of carbon, whose composition corresponded to the formula, $Fe_{2.28}C$.[110]

Carburization of the KWI normal iron catalyst with CO at 0.1 atm pressure, a flow rate of 8 l per 10 g Fe per hr, and a temperature of 325°C for 5 hr produced chiefly magnetite (Fe_3O_4). At the end of a

total of 12 hr, the catalyst consisted of 50 per cent magnetite and 50 per cent of a carbide whose Curie Point (CP) was 265°C. This ratio of magnetite:carbide remained constant even after carburization for 13 hr longer. Recent x-ray diffraction and thermomagnetic analyses in the U. S. Bureau of Mines laboratory [145] showed that this carbide had the formula Fe_2C and was identical with the carbide reported by Hägg, CP 247°C.[146] In another experiment, the KWI normal iron catalyst was reduced with hydrogen at 250°C at 1 l per 20 g Fe per hr for 240 hr and then carburized with 1 l CO per 20 g Fe per hr for 219 hr at 220°C.[110] Again the catalyst consisted of 50 per cent magnetite and 50 per cent CP 265°C carbide. A carbide was produced when the Rheinpreussen precipitated iron catalyst of composition $100Fe:(0.2–0.5)Cu:1K_2CO_3$ was pretreated with an H_2-CO gas mixture.[147] This carbide, which was not definitely characterized at Rheinpreussen, was believed by U. S. Bureau of Mines investigators who later reviewed these experiments to be the Hägg carbide.[145] The catalyst containing 1 per cent K_2CO_3 showed more carbide than that with 0.25 per cent added K_2CO_3, probably as a result of its stabilization by the presence of more alkali. In a U. S. Bureau of Mines test, a fused synthetic-ammonia-type catalyst, D3001, was reduced by hydrogen at 450°C and then carburized with carbon monoxide at 240°C for 539 hr. X-ray diffraction and thermomagnetic analyses showed that the Hägg carbide was produced by this treatment.[145] KWI tests made with a precipitated iron-copper catalyst of composition $100Fe:1Cu:1.5K_2CO_3$, prepared by adding the requisite amount of cupric nitrate to the preneutralized iron solution and carrying out the precipitation and subsequent treatment in the same manner used for the normal iron catalyst, showed the following results. Carburization with CO at 0.1 atm, a flow rate of 8 l per 10 g Fe per hr, and a temperature of 325°C produced in 0.5 hr the same result that was produced in 12 hr in the normal iron catalyst, *ie*, 50 per cent magnetite-50 per cent CP 265°C carbide. At the end of 5 hr, chiefly CP 265°C carbide was present and very little magnetite. After 25 and 62 hr, no additional change in the product was observed. Similarly, when pretreatment was done with water gas ($1CO + 1H_2$) for 25 hr at 325°C, 0.1 atm, and a space velocity of 8 l per 40 cc catalyst per hr, the CP 265°C carbide predominated. This catalyst showed a contraction of 49 per cent within 5 days, when taken into synthesis at 215°C and 12 atm.

The presence of a small amount of another carbide was also detected

[145] L. J. E. Hofer, E. M. Cohn, and W. C. Peebles, *J. Am. Chem. Soc.*, **71**, 189–95 (1949).

[146] G. Hägg, *Z. Krist.*, **89**, 92–4 (1934).

[147] F.I.A.T. Reel 116-X, Frames 1,673–83.

at KWI in the 100Fe:1Cu:1.5K_2CO_3 catalyst carburized as described above with CO or 1CO + 1H_2. This additional carbide was observed in significant quantity when a sample of the same catalyst was reduced with hydrogen at 250°C for 240 hr at a space velocity of 1 l per 40 cc (20 g) Fe per hr and then carburized with CO at 220°C for 219 hr. Thermomagnetic analysis showed that this catalyst contained, in addition to the CP 265°C carbide, a carbide whose Curie Point was 380°C. The identity of the CP 380°C carbide with that of the hexagonal close-packed carbide (Fe_2C) reported by Halle and Herbst [148] was established in the U. S. Bureau of Mines laboratory.[145] Similarly, a KWI catalyst of composition 100Fe:1Cu:0.25K_2CO_3 produced largely the CP 380°C phase when carburized at 205°C. X-ray studies in the I.G. Oppau ammonia laboratory [110] showed the presence of the hexagonal iron carbide, Fe_2C, in Fe-Cu-Al_2O_3-K_2O and Fe-Cu-MgO-K_2O precipitated catalysts that had been carburized for several hours at 240°C with CO-H_2 mixture or at 220°C with CO alone. Detailed analysis of the lines showed a hexagonal lattice (lattice constants, $a = 2.8$, $c = 4.6$, $c/a = 1.63$) whose similarity with that of iron nitride, Fe_2N ($a = 2.7$, $c = 4.4$, $c/a = 1.62$), indicated the existence of the hexagonal iron carbide, Fe_2C. The hexagonal iron carbide was also identified in a U. S. Bureau of Mines precipitated iron catalyst, 100Fe:10Cu:0.32K_2O, which had been reduced in hydrogen at 220°C and then carburized with carbon monoxide at 188°C.[145]

Thermomagnetic analysis of a catalyst of which the composition was 75Fe^{+2}:25Fe^{+3}:20Cu:1.5K_2CO_3 was reported by Pichler and Merkel.[110] After pretreatment at atmospheric pressure of 1CO + 2H_2 gas at an hourly space velocity of 500 and a temperature of 225°C, it was observed that both the CP 265°C and CP 380°C carbides were present in the catalyst. Another sample of this catalyst, pretreated under the same conditions and then used in synthesis for 2 days at 220°C, atmospheric pressure of water gas, and an hourly space velocity of 100, showed an increase in the content of the CP 380°C phase, so that the two carbides were present in a 1:1 ratio. X-ray studies were made at the I.G. Farben. ammonia laboratory at Oppau on a sample of used (in the Fischer-Tropsch synthesis) synol catalyst, identified as WK 17 and containing by analysis 86.62 per cent Fe, 3.42 Al_2O_3, 0.44 K, and 2.58 Ca. The hexagonal iron carbide (Halle and Herbst carbide) and a small amount of Hägg carbide were observed to be present.[148]

Pichler and Merkel [110] were of the opinion that the hexagonal carbide was characteristic of a catalyst suitable for synthesis at atmsopheric

[148] T.O.M. Reel 26, Bag 2,463, Group Leader Conference, Ludwigshafen; T.O.M. Reel 134, Item H.10, Report by Dr. Wenzel.

pressure and that the formation of the hexagonal carbide was favored by pretreatment with hydrogen, carburization at low temperatures, and the presence of copper. However, copper was not present in the synol catalyst (Table 84), which contained hexagonal carbide. It was Halle's opinion [148] that the hexagonal carbide was unstable at temperatures above about 300°C and that, consequently, pretreatment at higher temperatures produced Hägg carbide. Rapid thermomagnetic measurements made at the U. S. Bureau of Mines [145] showed that the hexagonal carbide (CP 380°C) was converted at 380°C to the Hägg carbide (CP 247°C). The Hägg carbide was decomposed at a high temperature (580°C) to cementite and free carbon, according to the equation:

$$\underset{\text{Hägg carbide}}{3Fe_2C} \rightarrow \underset{\text{cementite}}{2Fe_3C} + \underset{\text{free carbon}}{C}$$

The presence of copper increased the temperature above which the hexagonal carbide decomposed; this temperature was increased by 50°C when the copper content was 2–3 per cent and by 100°C when the copper content was 7 per cent.[148] However, the work of Hofer, Cohn, and Peebles [145] led them to believe that the hexagonal carbide may have been present in other copper-free catalysts reported in the literature, but that it was not recognized. Hexagonal carbide has not been found in fused catalysts used in synthesis tests at the U. S. Bureau of Mines. In test X-194 [149] fused synthetic-ammonia-type catalyst D-3001 (6–8 mesh) was reduced with hydrogen at 1 atm, an hourly space velocity of 2,500 for 40 hr at 450°C. It was tested in the synthesis with $1H_2 + 1CO$ gas at 7 atm for 1,875 hr at an average temperature of 257°C. Samples removed periodically and subjected to x-ray and thermomagnetic analysis showed that metallic iron was rapidly converted to Hägg carbide in the first few days of the synthesis, the carbide content reaching a maximum of 30 per cent iron as Hägg carbide at 200 hr. In subsequent testing at this temperature the iron as Hägg carbide decreased slowly to 20.5 per cent at 1,875 hr. Magnetite was formed at a slower rate than carbide; however, in the course of the experiment the magnetite eventually increased to 40 per cent iron as magnetite. After 1,875 hr, the temperature was raised, and the composition began to change so that in the last operating period at 300°C 25 per cent of the Hägg carbide had been oxidized. At the end of this period the converter was found to be plugged.

Another pretreatment technique, in which catalysts are nitrided, is described in Chapter 6, p 549.

[149] R. B. Anderson, L. J. E. Hofer, E. M. Cohn, and B. Seligman, *J. Am. Chem. Soc.*, in press.

Reactivation of Iron Catalysts

Figure 47 shows the reactivating effect of hydrogen upon a comparatively poor KWI precipitated catalyst taken into synthesis at 235°C and 15 atm of $3CO + 2H_2$ gas, at a flow rate of 4 l per hr.[102] A contraction of 50 per cent was obtained for 2 days and 47 per cent on the third day. The dotted portion of the curve shows that the contraction would have

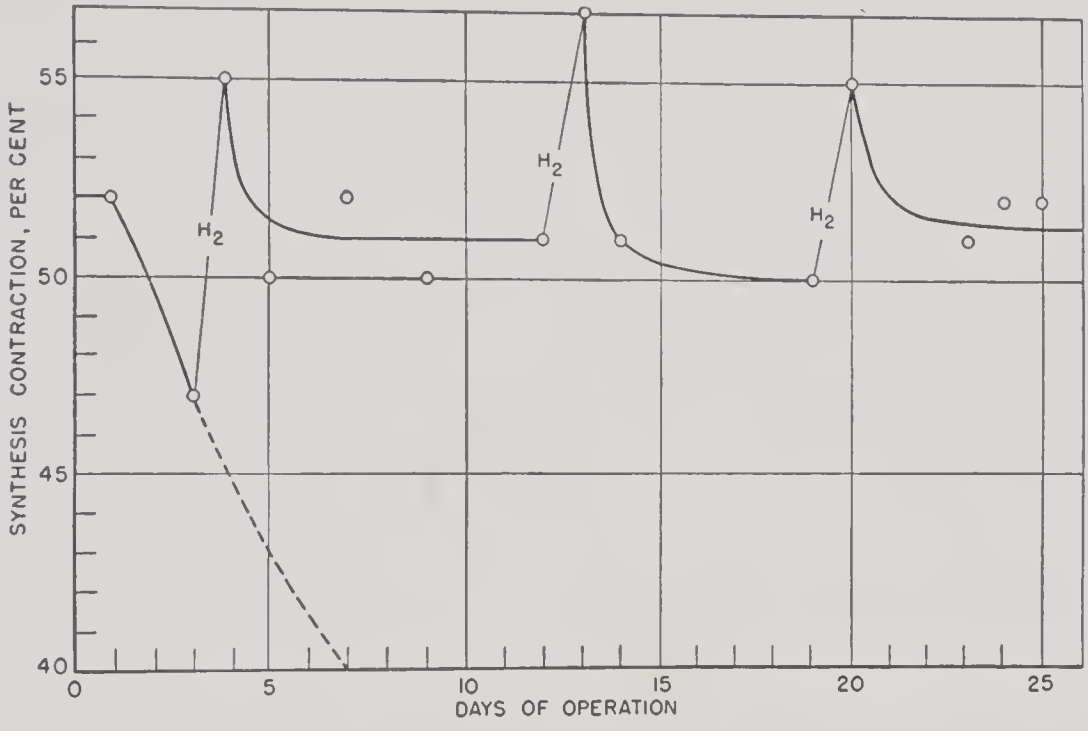


Figure 3–47. Influence of H_2 on the activity of precipitated iron catalyst in the medium-pressure synthesis (KWI). Reproduced from reference 102.

dropped to 40 per cent by the end of 7 days. However, on the third day, the catalyst was treated with hydrogen for 15 hr at 8 l per hr, atmospheric pressure, and 325°C. Subsequently, reactivation twice more at intervals during the test permitted operation of the catalyst at 235°C for more than 2 months. Reactivation by this procedure was reported to be ineffective if the catalyst had been in operation a long time or if the contraction had dropped below 45 per cent.

The effect of reactivation of iron-copper decomposition catalysts by using ammonia in the water gas was reported by Fischer [7] to be only temporary; it appeared to increase gaseous hydrocarbon production. When synthesis was carried out with ammonia in the water gas (up to 1.5 volume per cent) oil production decreased.

SCHWARZHEIDE TESTS

A sharp curtailment in the German cobalt supply, most of which was imported from the Belgian Congo, was caused by the outbreak of World War II. This situation resulted in an intensification of the research on iron catalysts which was in progress in six different organizations—Kaiser Wilhelm Institut für Kohlenforschung (KWI), Lurgi, Ruhrchemie, Rheinpreussen, I.G. Farbenindustrie, and Brabag—each trying to develop the "best" catalyst. When the cobalt shortage became acute, it became necessary to modify the objective from the development of a catalyst for use in projected new plants to one that could be substituted for cobalt in the existing medium-pressure plants. Because of the wide differences in research on iron catalysts conducted by the six companies, it is not surprising that the Reichsamt für Wirtschaftsausbau had difficulty in deciding which was the most promising catalyst with which to replace cobalt in the commercial plants. Consequently, the Reichsamt arranged a comparative experiment, the "Reichsamtversuch," at the Braunkohle-Benzin A.G. plant in Schwarzheide-Ruhland. In these tests, which started in September 1943 and lasted for 3 months, the "best" catalyst submitted by each organization was tested simultaneously with the others.[29]

Each catalyst in the Reichsamtversuch comparative test was operated in a pilot-plant unit which had a catalyst capacity of 5 l and consisted of a single tube of the standard middle-pressure reactor, as built by Gutenhoffnungshutte. The annular layer of catalyst had a diameter of 24 mm I.D., 44 mm O.D., and a depth of 5 m. The tube was water-jacketed, with a vapor chamber connected to the top, by means of which the steam temperature could be controlled to give the desired synthesis temperature. A description of the catalysts tested and of the results obtained is presented in the following pages. The characteristics necessary for successful operation on the large scale were (1) high degree of conversion to non-gaseous products with a low degree of gas production, particularly methane; (2) H_2:CO use ratio closely approaching the H_2:CO ratio of the process gas, to permit satisfactory operation of further stages of synthesis; (3) high yield of the desired products per unit weight of catalyst; and (4) catalyst stability. These characteristics were not demonstrated by any of the catalysts and the results were inconclusive.

Catalysts

The compositions of the catalysts submitted by each of the six organizations for the cooperative tests are shown in Table 85.[29,150] The KWI

Table 85. Catalysts Used in Cooperative Tests at Schwarzheide

Company	Parts per 100 Parts of Iron			Apparent Density, g per cc	Reduction (Induction)
	Copper (Zinc) [Other]	K_2CO_3	Carrier		
Kaiser Wilhelm Institut für Kohlenforschung	1	0.75	None	1.02	Water gas, 325°C, 0.1 atm, 24 hr
Lurgi	10 [$9Al_2O_3$]	2 [a]	$30SiO_2$	0.79	H_2, 280°C, 30 per cent reduction
Brabag	20 (20)	1	None	1.37	Water gas, 235°–240°C, 48 hr
I.G. Farben.[b]	....	....	....	2.27	H_2, 500°C
Ruhrchemie	5 [$10CeO_2$]	....	50 kieselguhr	0.44	H_2, 300°C
Rheinpreussen	7.5	2	50–65 powdered dolomite	0.68	H_2, 300°–400°C (water gas, 245°C)

[a] K_2O. [b] Contained $Al_2O_3 + CaF_2 + K_2O$.

catalyst was precipitated from a warm nitrate solution (60°–70°C), containing ferrous and ferric ions in a ratio of approximately 1:1 and 1 per cent copper, by a boiling solution of sodium carbonate.[32] The slurry was heated to 100°C for a few minutes, then filtered, and washed with hot distilled water until free from alkali. A paste was made with distilled water, and a solution of potassium carbonate was mixed with the paste. The first catalyst, containing 0.25 per cent K_2CO_3, based on the iron, gave too much liquid and gaseous products because the experimental reactor used at Schwarzheide had an annular space wider than those usually employed at the KWI.[29] This difficulty was overcome by increasing the alkali content in the second catalyst to 0.75 per cent K_2CO_3. The paste was thickened on a water bath and dried at 110°C for 24 hr. The dried pieces were broken into 2–4-mm granules, which were pretreated by the passage of 0.1 atm of water gas at 325°C for 24 hr (4 l gas, based on 1 atm, per 10 g Fe per hr). The strongly pyrophoric catalyst was then soaked in paraffin wax to protect it from oxidation and put into the converter with as little contact with air as possible. At the beginning of the synthesis, the catalyst was very active at 185°–190°C.

[150] T.O.M. Reel 134, Section 1B, Item 24.

In order to maintain a high conversion throughout the 3-month test, the temperature was raised gradually from 195° to 224°C, most of the operation being conducted between 215° and 220°C.

Preparation of the Lurgi catalyst is the same as that described on p 270 of this chapter. The alkali silicate in the Lurgi catalyst, *ie*, K_2O + equivalent amount of silica, was thought to be responsible for the mechanical strength of the catalyst and its long life. During the 90-day run at Schwarzheide, the temperature had to be raised only 2°, from 216° to 218°C, to maintain activity.[29] Later tests showed that the use ratio of H_2:CO could be improved from 0.7 (without recirculation or 1.0 with recirculation) to 1.3 by increasing the copper content to 25 per cent.[29] The Brabag catalyst was a normal precipitated preparation, made from the nitrates and sodium carbonate.[29,39] The first of these used in the Reichsamtversuch was too soft and disintegrated, probably because of insufficient pretreatment. The second attempt was spoiled because the temperature was increased too rapidly and deposition of carbon occurred. The third catalyst was successful. The I.G. Farben. (Ludwigshafen) catalyst was a fused Fe-Al_2O_3-CaF_2-K_2O preparation, probably reduced in hydrogen at a high space velocity and temperature of 500°C.[29,70] The calcium fluoride was added to increase the production of light hydrocarbons, while operating at a low temperature. It is of interest to note that such a catalyst was just as active as the other catalysts used in the Reichsamtversuch, all of which were made by precipitation and pretreatment under carefully controlled conditions. The Ruhrchemie catalyst,[35] which was precipitated on kieselguhr, was probably prepared by a procedure similar to that described on p 263, this chapter. Rheinpreussen's catalyst was a less effective catalyst of the type whose preparation is described on p 268, this chapter.[29,32,38,39] The Rheinpreussen catalyst encountered "coking" difficulties and had to be renewed four times.

Results of Tests

Because the objective was to replace cobalt catalysts in existing plants, the highest permissible temperature in these tests was 225°C, and the operating pressure was 10 atm of $1.25H_2$ + 1CO gas (containing 12 per cent inert gas). The analysis of the synthesis gas showed that it contained 6.2 volume per cent CO_2, 39.2 CO, 48.8 H_2, 2.6 CH_4, and 3.2 N_2. Temperature and space velocity were independently varied by each operator to secure optimum yields and durability. At the end of 2 weeks all units had reached about 200°C. Space velocities were in the range 105–110 volumes of synthesis gas per volume of catalyst per hour. The performance data and product distribution for each of the six

TABLE 86. COOPERATIVE TESTS ON IRON CATALYSTS AT SCHWARZHEIDE

[10 atm, 200°–225°C; synthesis gas was 88 per cent $1CO + 1.25H_2$ and 12 per cent inerts. Space velocity was volumes (NTP) of feed gas per volume of catalyst per hour.]

	KWI	Lurgi	Brabag	I.G. Farben.	Ruhr-chemie	Rhein-preussen
Space velocity	109	107	111	115	104	104
CO converted, per cent	85	88	77	81	70	62
$CO + H_2$ converted, per cent	69	65	58	63	54	57
Use ratio, $CO:H_2$	0.80	0.66	0.69	0.74	0.72	1.07
Maximum yield, g per cu m [a]	147	142	141	144	147	168
Average yield, g per cu m [a]	125	124	108	117	103	104
Average yield, tons per day	3.26	3.19	2.88	3.23	2.57	2.60
C_5+, kg per hr per cu m of catalyst	10.9	11.6	10.8	10.9	8.8	8.5

[a] Grams per cubic meter $CO + H_2$ gas.

TABLE 87. COOPERATIVE TESTS ON IRON CATALYSTS AT SCHWARZHEIDE, PRODUCT DISTRIBUTION IN WEIGHT PER CENT

(Figures in parentheses are percentage of olefins in the fraction.)

	KWI	Lurgi	Brabag	I.G. Farben.	Ruhr-chemie	Rhein-preussen
Wax	18.1	35.2	43.0	21.0	25.6	13.1
(olefins)	(2)	(13)	(11)	(12)	(8)	(2)
Diesel, C_{11}–C_{18}	14.2	13.2	16.3	11.2	12.8	13.5
(olefins)	(15)	(39)	(47)	(45)	(23)	(19)
Gasoline, C_5–C_{10}	25.0	19.4	17.6	25.4	22.2	29.6
(olefins)	(48)	(51)	(67)	(59)	(44)	(48)
$C_3 + C_4$	19.8	12.2	10.6	18.6	14.5	21.5
(olefins)	(53)	(66)	(76)	(71)	(62)	(53)
C_2H_4	0.9	2.7	2.2	2.8	2.2	0.7
C_2H_6	7.8	2.6	2.3	4.9	4.4	8.1
CH_4	8.0	5.6	3.8	9.0	7.0	8.1
$C_1 + C_2 + C_3$ alcohols	6.1	9.1	4.2	7.1	11.3	5.4

catalysts are summarized in Tables 86 and 87, respectively, and in Figure 48.[32,38,39,150] The highest wax yields (see Table 86 and Figure 48) were obtained from the Lurgi and Brabag catalysts, whereas the Rheinpreussen catalyst had the lowest yield of wax. The Diesel oil yield was lower than the gasoline yield for all the catalysts.

None of the catalysts tested combined all the features desired, and the order of merit in which the catalysts are placed depends on the par-

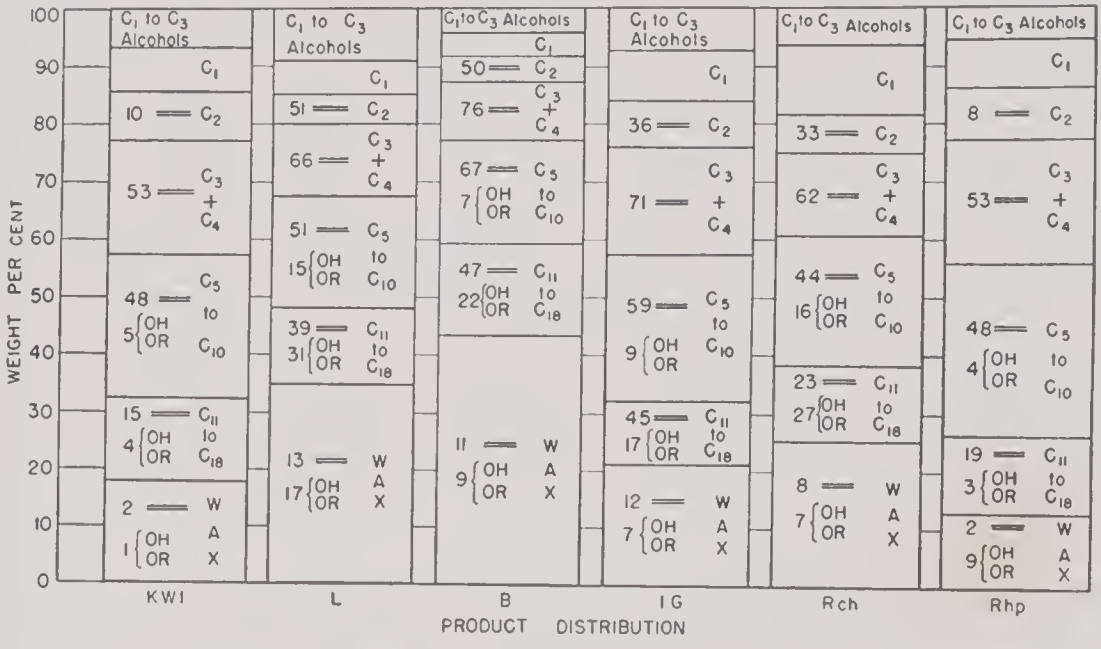


FIGURE 3–48. Cooperative tests on iron catalysts at Schwarzheide == = Olefins, OH = Alcohols, OR = Esters, KWI = Kaiser Wilhelm Institute, L = Lurgi, B = Brabag, I.G. = I.G. Farben, Rch = Ruhrchemie, Rhp = Rheinpreussen. Reproduced by permission from *Chem. Eng. Progress*, **44**, 472 (1948).

ticular feature used as criterion. It is obvious that catalysts for large-scale use must be reasonably consistent in behavior; in this connection, it is important to note that only the Lurgi, I.G. Farben., and Ruhrchemie catalysts operated 90 days with one filling of catalyst. A second Reichsamtversuch was started, which had as its objective the investigation of the effect of recirculation.[35] The Ruhrchemie catalyst had the composition 100Fe:5Cu:10CaO:50 kieselguhr, containing 270 g Fe per l of catalyst. Only one other firm, which Roelen [35] thought was I.G. Farben., took part in the second Reichsamtversuch; it was cut short after 170 hr.

Ruthenium Catalyst Studies

The use of ruthenium as a catalyst for the production of high-melting wax from carbon monoxide and hydrogen was studied at the KWI for several years (1938–1941). The process is mostly of theoretical interest

because of the high cost of ruthenium and the small commercial demand for the very high-molecular-weight paraffins produced by synthesis over ruthenium. Investigation was not carried out beyond the laboratory stage.[32,38,39]

PREPARATION

The catalyst was prepared in a silver crucible by melting commercial ruthenium powder with potassium hydroxide and potassium nitrate in the proportions of 1 part ruthenium to 10 KOH and 1 KNO_3. The potassium nitrate was added in small portions. Fusion was complete within 2 hr. After cooling, the fused mass was dissolved in water; a deep red solution of potassium ruthenate resulted, which was heated to boiling. Dropwise addition of methyl alcohol precipitated ruthenium dioxide (RuO_2), which was filtered on a fritted glass plate and washed, first with water acidified with nitric acid and then with distilled water. The filter cake was dried at 110°C. The oxide was reduced with $2H_2 + 1CO$ gas at atmospheric pressure and 150°C. Other methods of preparation were possible, but it was essential that ruthenium be present in as great dispersion as possible. Carriers, such as kieselguhr, and added alkali were apparently without effect.

PROCESS CONDITIONS

Optimum synthesis conditions were 195°C and 100 atm of $2H_2 + 1CO$ gas passed at a rate of 1 l per g Ru per hr. The average yield from one-stage operation under these conditions was reported to be 100 g of solid paraffin and 50 g of oil per cu m of $2H_2 + 1CO$ gas. Methane production was very small. After 560 days, when the temperature had been raised to 215°C, the yield was 140 g per cu m. The ruthenium catalyst was, however, even more susceptible to poisoning by sulfur than cobalt catalysts.

The yield increased with pressure and decreased with temperature. At pressures below 10 atm and temperatures of 200° or lower, no appreciable conversion of $CO + H_2$ to higher hydrocarbons resulted. Figure 49 shows the results obtained by Pichler and Buffleb [151] in experiments at pressures from 15 to 1,000 atm and at a temperature of 180°C. Three grams of ruthenium catalyst was used, and the flow of $2H_2 + 1CO$ synthesis gas was so adjusted that 1 l of effluent gas was obtained per hr. The throughputs of $2H_2 + 1CO$ (calculated from the nitrogen contents of the ingoing and effluent gases) were 1.08, 1.16, 1.79, 2.57, 5.0, and 5.26 l per hr per 3 g Ru for 15, 30, 50, 100, 180, and 1,000 atm,

[151] H. Pichler and H. Buffleb, *Brennstoff-Chem.*, **21**, 257–64, 273–80, 285–8 (1940).

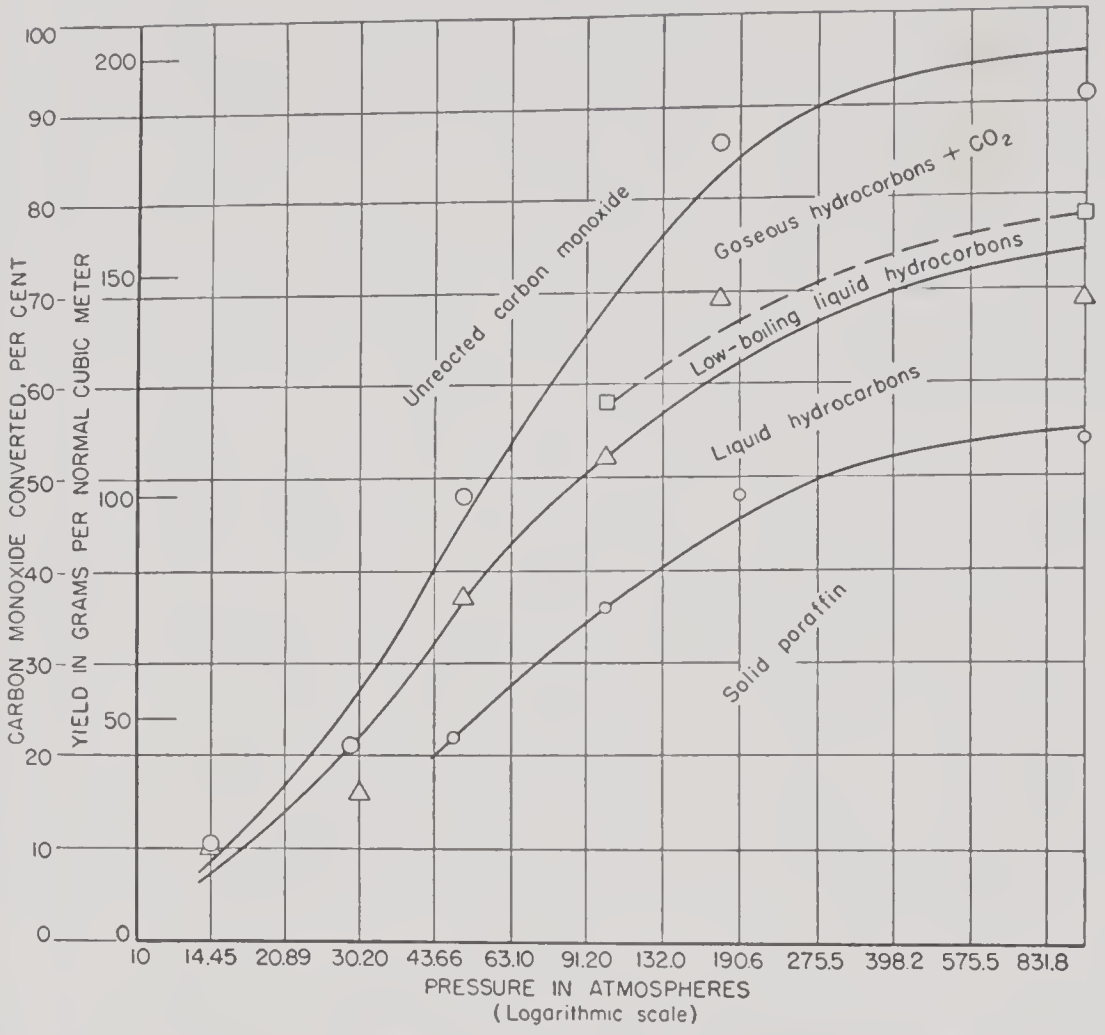


FIGURE 3–49. Yield and character of products at 180°C and various pressures, with ruthenium catalyst. Reproduced from reference 151.

respectively. The conversion to hydrocarbon increased rapidly with increasing pressure up to about 300 atm and more slowly above this pressure.

PRODUCTS

At all pressures, solid paraffinic hydrocarbons constituted at least 60 per cent of the total yield of liquid + solid hydrocarbons. At 1,000 atm and 180°C, 57 per cent of the carbon monoxide was converted to solid paraffin wax and the latter was 71 per cent of the liquid + solid product. The fraction of gaseous hydrocarbons in the products was approximately 25 per cent for all pressures. It is interesting to note that, whereas for a cobalt catalyst about 95 per cent conversion was reached at 15 atm, for a ruthenium catalyst 95 per cent conversion necessitated a pressure of about 300 atm.

Waxes from the ruthenium synthesis melted in the range 50°–135°C

and had molecular weights as high as 23,000. Sixty-five per cent of the product obtained at 100 atm pressure was snow-white wax in the crude state, melting at 118°–120°C. Solvent extraction of the solid product obtained at 1,000 atm pressure resulted in the fractions described in Table 88. One-third of the product had an average melting range of 51°–57°C; 14–17 per cent, 92.5°–95°C; and approximately 50 per cent, above 120°C.

TABLE 88. SOLVENT EXTRACTION OF WAX FROM RUTHENIUM SYNTHESIS AT 1,000 ATM [a]

Extraction Conditions			Melting Range, °C	Physical Properties				
				Density		Av. Molecular Weight	Viscosity, Centistokes	
Solvent	Temperature, °C	Per Cent Soluble		20°C	150°C		150°C	180°C
n-Pentane	34	30–33	51–57	.....	.....	.....	.....	.....
n-Hexane	68	14–17	92–95	.....	0.765	760	6	4
Product fraction	90	14–16	121–122	0.966	0.778	1,750	29	17
n-Heptane	98	20–25	129–130	0.978	0.783	6,750	870	410
Product fraction	121	12–15	132–134	0.980	0.786	23,000	35,600	15,800

[a] Reference 32.

Poisoning Effect of Sulfur

All the catalysts used in the synthesis of higher hydrocarbons from hydrogen and carbon monoxide are very readily poisoned by sulfur. Thus, the activity of precipitated nickel-manganese-thoria and nickel-manganese-kieselguhr catalysts was reduced 50 per cent by 17 and 135 mg, respectively, of hydrogen sulfide per g of nickel. The reported tolerance for carbon disulfide of the same catalysts is much larger than that for hydrogen sulfide.[152] A similar report of a large tolerance for organic sulfur as compared with hydrogen sulfide was given by King and Myddleton [153] for precipitated cobalt-thoria-kieselguhr (100:18:100) catalyst. When carbon disulfide was added to the feed gas over a period of 4 days to an extent corresponding to 33 mg of sulfur per cc of catalyst, it was necessary to raise the temperature progressively from 185° to 210°C. King stated that at the space velocity used (190 volumes per volume of catalyst per hour) the degree of fouling corresponded to about

[152] K. Fujimura, S. Tsuneoka, and K. Kawamichi, *J. Soc. Chem. Ind. Japan*, **37**, Suppl. Binding, 395–400 (1934).

[153] J. G. King, *J. Inst. Fuel*, **11**, 484–5 (1938); W. W. Myddleton, *J. Inst. Fuel*, **11**, 477–84 (1938).

TABLE 89. EFFECT OF SULFUR (30 G S PER 100 CU M) IN THE SYNTHESIS GAS

(Ni-Co-Si skeletal catalyst, 4 l synthesis gas per 5 g catalyst per hr.)

Test Period	Reactivation Treatment of Catalyst,[a] hr	Cumulative Time in Test Period, hr	Age of Catalyst, hr	Amount of S Added, mg per g Ni + Co	Contraction, per cent	Yield,[b] cc per cu m $2H_2 + 1CO$		
						Gasoline	Diesel Oil	Total
1	None	1			57			
		27		5.5	39	36	40	76
		47	47	11.3	29			
2	0.5	3			53			
		27		18.5	32	26	29	55
		48	95	22.8	27			
3	2	1			51			
		22			27	25	15	40
		40	135	32.4	15			
4	16[c]	1			14			
		47	182	43.7	9	9	6	15
5	2	2			18			
		44			8			
		93			6			
		165			4			
		334	516	123.8	1.5	..	..	..
6	16	1	517	124.3	3	..	..	..

[a] Boiled in sodium hydroxide.

[b] Yield was 90 cc when pure synthesis gas was used.

[c] Extracted with Fischer-Tropsch gasoline fraction.

10 years' working at the concentration of sulfur (2 mg per cu m) usually accepted as the highest permissible. Fischer and Meyer [154] reported a rapid deactivation of nickel-cobalt-silica skeletal catalyst in the presence of unpurified synthesis gas containing about 30 g of sulfur per 100 cu m of gas. Under normal conditions, the liquid hydrocarbon yield decreased about 25 per cent in 17 days; in the presence of the sulfur-containing synthesis gas, the yield decreased 23 per cent in 2 days. From the data

[154] F. Fischer and K. Meyer, *Brennstoff-Chem.*, **15**, 107–10 (1934).

summarized in Table 89, it was calculated that the yield was decreased 39 per cent by 18.5 mg sulfur per g of nickel plus cobalt in the catalyst (*ie*, in 3 days).

Fujimura and his coworkers [152] reported that the initial effect of small amounts of hydrogen sulfide was to increase the catalyst (nickel-manganese) activity. This was confirmed by Herington and Woodward [155] for cobalt-thoria-kieselguhr (100:18:100) catalysts. Hydrogen sulfide was mixed with the synthesis gas in small measured batches. No hydrogen sulfide was eliminated in the off gas during the course of the sulfur-poisoning experiments. The results are given in Table 90. The

Table 90. Effect of Hydrogen Sulfide on Yield [a]

Amount of Sulfur Added, mg per g catalyst	Catalyst Temperature, °C	Ratio of Hydrocarbon Yield to Corresponding Yield before Addition of Sulfur	
		Condensed Oil	Hydrocarbons in Off Gas, $C_{1.7}H_{5.7}$
0	183	1.0	1.0
0.67	183	2.3	1.0
3.50	183	2.1	0.8
7.94	183	...	0.5
7.94	195	2.0	1.3
13.4	195	1.5	...
33.5	207	1.2	2.1

[a] Reference 155.

first additions of sulfur caused a marked increase in the yield of liquid hydrocarbons at constant reaction temperature. There was, however, an immediate falling off in the yield of gaseous hydrocarbons. The total hydrocarbon yield increased until more than 8 mg of sulfur had been added to each gram of catalyst. Further additions of hydrogen sulfide caused a drop in total hydrocarbon yield, but, as shown in Table 90, this could be offset by raising the reaction temperature rather more rapidly than would normally be necessary in the absence of hydrogen sulfide. The higher temperatures favored the production of lighter hydrocarbons, but even so, after the addition of as much as 33.5 mg of sulfur per g of catalyst, the yield of liquid hydrocarbons was still 20 per cent greater than before the addition of sulfur. Further additions of sulfur resulted in a continuous decrease in activity until complete poisoning was reached.

[155] E. F. G. Herington and L. A. Woodward, *Trans. Faraday Soc.*, **35**, 958–67 (1939).

Contrary to the above observations on the poisoning effect of sulfur in the Fischer-Tropsch synthesis is a patent published in 1949 describing an operation with a catalyst containing sulfur.[156] At 530°F, 200 psig of $2H_2 + 1CO$, and a space velocity of 183, a molybdenum disulfide catalyst alkalized with 2–3 per cent of KOH produced 69 per cent conversion of CO, of which 30 per cent was converted to C_3+ hydrocarbons and organic oxygenated compounds. The product was low boiling; fractional distillation of the liquid products resulted in the following values, in mole per cent: 1 C_3, 11 C_4, 22 C_5, 22 40–57°C, 29 57–67°C, 4 71–85°C, and 11 >85°C.

Summary

The first Fischer-Tropsch catalyst was reported by Fischer in 1925. It was prepared by reduction at 400°C of a mixture of equal parts by weight of commercial iron oxide (obtained from the oxalate) and zinc oxide. The latter component, a difficultly reducible compound, was incorporated into the catalyst to prevent sintering of the active constituent during reduction. Hydrocarbons of molecular weight larger than methane were present in the product gas obtained when $3H_2 + 1CO$ gas mixture was passed over this catalyst at atmospheric pressure and at a temperature of 370°C. Within the next few years an enormous amount of catalyst testing was done with iron, cobalt, and nickel catalysts combined with difficultly reducible oxides or easily reducible oxides (such as copper) or both types of oxides. However, very slight progress was made toward the achievement of a commercially suitable catalyst.

Precipitation of nickel-thoria on kieselguhr by Fischer in 1931 and preparation of the corresponding cobalt catalyst ($100Co:18ThO_2:100$ kieselguhr) in 1932 paved the way for the development of the Ruhrchemie commercial catalyst. The cobalt catalyst was precipitated on the carrier, kieselguhr, in order to overcome the disadvantages of dense catalyst granules. If the reaction is highly exothermic, as in the Fischer-Tropsch synthesis, the heat produced by a dense, unsupported catalyst may exceed the capacity of the reactor to remove the heat of reaction, and the catalyst may be quickly destroyed. Tests showed that the role of the kieselguhr was important in two respects: (1) It produced the proper degree of dispersion of the active metal and the desired porosity of the catalyst granules, and it provided a framework which prevented a large decrease in bulk volume during reduction. In addition, (2) it influenced the yields and life of the catalyst. Experiments on the effect of the physical and chemical nature of the kieselguhr on the activity of

[156] S. Grant Stewart (to Phillips Petroleum Co.), U. S. Patent 2,490,488, Dec. 6, 1949.

the cobalt catalyst showed that use of the acid-washed, natural (not calcined or flux-calcined at high temperature) product yielded the most active catalyst.

Because of difficulties encountered in operation with Fischer's Ni-MnO-Al_2O_3-kieselguhr catalyst, nickel was abandoned for commercial use. The first satisfactory catalyst used in the Ruhrchemie pilot-plant units contained approximately 100Co:18ThO_2:200 kieselguhr:2Cu, parts by weight. The advantage of incorporating a small amount of copper into the catalyst was that it made possible the use of a low reduction temperature. However, the life of the copper-containing catalyst was relatively short, and copper was eliminated from the catalyst when a separate reduction unit was completed at Ruhrchemie late in 1935. The standard, or normal, commercial catalyst in 1937 had the approximate composition 100Co:18ThO_2:200 kieselguhr, which was changed in 1938 to 100Co:15ThO_2:200 kieselguhr. Replacement of part of the thoria by magnesia resulted in the normal German commercial catalyst, which had the following composition: 100Co:5ThO_2:8MgO:200 kieselguhr. It was used from 1938 until 1944, when synthetic oil and wax production was sharply curtailed as a result of intensive bombing of the plants. The same composition was found to be best for both atmospheric- and medium-pressure synthesis and to produce catalysts that had a life of about 6 months.

In the preparation of the commercial catalyst, a hot solution of the nitrates of cobalt, thorium, and magnesium was mixed with a hot sodium carbonate solution. The required amount of dry kieselguhr was immediately stirred in, and the slurry was filtered and washed with hot distilled water. The washed cake was extruded, and the product was dried and screened. The finished catalyst, obtained in 1–3-mm granules, was reduced in thin layers by a rapid stream of hot, dry hydrogen containing 25 per cent nitrogen.

The average yield obtained in synthesis on this catalyst was 150 g per cu m of sulfur-free $2H_2 + 1CO$ gas, of hydrocarbons ranging from propane-propylene to waxes of 2,000 molecular weight. In addition, about 25 g of C_1–C_2 hydrocarbon gases was produced. The average distribution of the liquid and solid products obtained in the Ruhrchemie process is as follows, in weight per cent: gasoline, 35–60; Diesel oil, 30–35; wax, 10–30, depending upon the pressure. The paraffin fraction was of considerable importance in Germany during World War II as raw material for the manufacture of synthetic detergents, soaps, and lubricants. Laboratory tests revealed that the composition of the catalyst also influenced the distribution of the products. The presence of manganese and a low kieselguhr content favored the production of high

wax yields. Roelen reported in 1940 that a cobalt catalyst whose composition was 100Co:15Mn:12.5 kieselguhr was active in the medium-pressure synthesis at 165°–170°C and produced large quantities of solid paraffin. In a 5-month test, the average wax fraction (br > 320°C) was 70 per cent of the total liquid-plus-solid hydrocarbon product. Large wax fractions were also obtained when the catalyst contained a high thoria concentration. However, these catalysts were unsuitable for commercial use for several reasons, the most important of which was rapid carbon deposition on the catalyst and concomitant deterioration of the catalyst. Cobalt catalysts containing nickel and large amounts of kieselguhr produced large oil fractions in the product. The disadvantages of these catalysts were (1) high yields of methane and other gaseous hydrocarbons, and (2) low total yields.

Although the cobalt catalyst was used in the German plants because its development occurred earlier than that of the iron catalysts, research on iron catalyst in the laboratory and pilot plants was continuously being done and is still in progress. Important advantages of iron over cobalt are that (1) it imparts flexibility to the Fischer-Tropsch process, and (2) it is easily available from many sources, whereas the supply of cobalt is limited.

Significant improvement in catalyst activity and life of iron catalysts was produced by the addition of alkali. The effect of alkali in producing higher-molecular-weight products had been observed when the synthol process was discovered. The same effect was observed in the Fischer-Tropsch synthesis on alkalized iron catalysts. With increasing alkali content of the catalyst, a large yield of paraffin wax is possible. For example, from a precipitated iron catalyst containing 1.3 per cent of added K_2O based on iron, Pichler reported that 42 per cent of the hydrocarbon product was paraffin wax. However, catalysts containing such large amounts of alkali were short-lived. The optimum alkali content, with respect to the life of the catalyst, was observed by U. S. Bureau of Mines workers to be 0.6 part of K_2O per 100 parts of Fe. Catalysts containing this quantity of alkali were operated at temperatures of about 230°C and showed no disintegration upon removal from the reactor. Other data indicated that alkalization of iron catalysts favored the production of oxygenated constituents in the liquid hydrocarbon fractions and a slight decrease in use ratio of H_2:CO.

The second important advance in the development of Fischer-Tropsch iron catalysts was the discovery of the medium-pressure synthesis. The best iron catalyst developed at the Kaiser Wilhelm Institut für Kohlenforschung (KWI) by Fischer up to 1930 was an alkalized iron-copper preparation made by decomposition of the nitrates and tested at atmos-

pheric pressure. The life of such a catalyst was only about 8 days. Within the next 5 years, the life of precipitated iron catalysts, when tested at atmospheric pressure, was increased to about 5 weeks. In 1937, a precipitated iron catalyst that had been under test for several weeks by Fischer and Pichler was put under 15 atm pressure; the yield was almost doubled and the life of the catalyst was increased substantially.

The development of pretreatment techniques was the third significant advance in the evolution of iron catalysts. It was preferable to pretreat fused, sintered, and "cemented" (iron oxide particles cemented into granules by the addition of a binding agent) catalysts by reduction with hydrogen at 450°C; however, induction with $1H_2 + 1CO$ gas at high temperatures produced satisfactory catalysts in instances in which induction was more desirable than reduction. Pretreatment of precipitated catalysts with CO or $H_2 + CO$ mixtures produced significantly better catalysts than reduction with hydrogen. Pichler reported that the optimum conditions for pretreatment of the normal KWI precipitated catalyst for operation at 15 atm of $3CO + 2H_2$ gas, 235°C, and throughput of 4 l per 10 g Fe per hr were the following: 0.1 atm CO, 325°C, and throughput of 4 l per 10 g Fe per hr, for 25 hr. Ruhrchemie found that pretreatment with water gas in place of hydrogen decreased methane formation; the advantage of carrying out the pretreatment with water gas at 0.1 atm could be reproduced by diluting the water gas with nitrogen and using a partial pressure of $H_2 + CO$ of 0.1 atm at a total pressure of 1 atm. U. S. Bureau of Mines induction of precipitated iron catalysts was done at atmospheric pressure of $1H_2 + 1CO$ gas, space velocity of 100, for 24 hr. When the catalyst contained less than 3 per cent of copper, based on iron, the temperature was 270°C; when the catalyst contained larger amounts of copper, the induction temperature was 230°C. Rheinpreussen reported a method of pretreatment in which $2H_2 + 1CO$ gas mixture was passed at 270°C over precipitated iron catalysts at atmospheric pressure and a throughput 20 times the normal synthesis gas rate.

X-ray diffraction and thermomagnetic analyses of iron catalysts carburized as described above revealed the presence of two carbides with the formula Fe_2C. One was identified as the Hägg carbide, and it had a Curie Point at 247°C; the other, the hexagonal close-packed carbide, had a Curie Point at 380°C. The latter carbide was converted at temperatures above 380°C to the Hägg carbide, which decomposed at a high temperature (580°C) to cementite and free carbon. U. S. Bureau of Mines investigators are of the opinion that iron catalysts pretreated at a low temperature contain principally the hexagonal carbide, whereas

pretreatment at high temperatures produces the Hägg carbide. The presence of copper apparently increases the temperature above which the hexagonal carbide decomposes; the decomposition temperature was increased by about 50°C when the copper content of the catalyst was 2–3 per cent and by 100°C when the copper content was 7 per cent.

Another pretreatment technique is nitriding, in which a catalyst reduced by hydrogen is converted to nitrides of iron by pretreatment with ammonia. From a nitrided fused synthetic-ammonia-type catalyst tested at 7 atm, the U. S. Bureau of Mines laboratory observed that virtually no wax was made; the product was of lower average molecular weight, containing larger yields of gaseous hydrocarbons, particularly methane, and of oxygenated molecules, than that obtained from similar, reduced catalysts. During synthesis, nitrided iron catalysts appear to resist oxidation and deposition of free carbon.

Because research on iron catalysts is still in progress and several Fischer-Tropsch processes are under development, it is impossible to select any one "best" preparation for commercial use. The problem is still further complicated by the economic situation. For example, the German economy is far different from that existent in the United States. Hence, the costs of synthesis gas production, operation of the synthesis, and catalyst manufacture must be weighed and balanced against each other in any particular situation. In addition, the distribution of products desired is influenced by the status of the petroleum and chemical markets.

An attempt was made in Germany in 1943 to select an iron catalyst that could be substituted for cobalt in the existing medium-pressure plants. A sharp curtailment in the German cobalt supply during World War II had resulted in intensive research on iron catalysts by six organizations. Because of the wide differences in the catalysts that had been developed, a comparative experiment, the Reichsamtversuch, was made in which each company submitted a catalyst. The catalysts were tested simultaneously for 3 months in pilot-plant units at the Braunkohle-Benzin A.G. plant in Schwarzheide-Ruhland. The characteristics necessary for successful operation on the large scale were (1) high degree of conversion to liquid products with a low degree of gas production, particularly methane; (2) H_2:CO use ratio closely approaching the H_2:CO ratio of the process gas, to permit satisfactory operation of further stages of synthesis; (3) high yield of the desired products per unit weight of catalyst; and (4) catalyst stability. None of the catalysts demonstrated all four characteristics, and the results were inconclusive.

In spite of the many operating and economic variables which influence the choice of catalysts for the Fischer-Tropsch processes, comparisons

of the modern iron catalysts are of interest. Evaluation of these catalysts may be made on the basis of the following criteria: (1) activity, life, and product distribution; (2) mechanical stability; and (3) economics.

An example of a highly active precipitated catalyst was $75Fe^{+2}$: $25Fe^{+3}$:20Cu:0.2K_2CO_3, parts by weight. In a 7-week test at 7 atm (gauge pressure) in the U. S. Bureau of Mines catalyst-testing laboratory, the average temperature was 229°C for 70 per cent conversion per pass and the yield, in grams per cubic meter of feed gas, was as follows: 9.4 CH_4, 33.5 C_1–C_4, and 105.7 C_3+ hydrocarbons. A Ruhrchemie precipitated catalyst, of composition 100Fe:5Cu:8CaO:30 kieselguhr, impregnated with 3–3.5 per cent of KOH, produced an average yield of C_2+ products of 106 g per cu m $1H_2 + 1CO$ at an average conversion of 65 per cent, when tested for 160 days at 10 atm of water gas with a recycle ratio of residual gas:fresh gas of 2.2:1. At the end of this time, the activity was still high at 220°C. The C_5+ hydrocarbon product contained 68 per cent of wax, of which 63 per cent was hard wax boiling above 460°C. The methane production was 7 per cent of the total CO + H_2 converted. A sample of a fused catalyst, the German synol catalyst, was tested at 7 atm in the U. S. Bureau of Mines laboratory for 8 weeks at an average temperature of 219.5°C for 70 per cent conversion per pass. The yield obtained was 7.4 g CH_4 per cu m of feed gas, 26.4 C_1–C_4, and 109.8 C_3+ hydrocarbons. Satisfactory activity was observed with a U. S. Bureau of Mines cemented magnetite ore catalyst, whose composition was 100Fe:3.5Al_2O_3:0.54K_2O. In an 8-week test at 7 atm pressure, the average temperature was 229°C for 70 per cent conversion per pass and the yield 6.9 g CH_4 per cu m of feed gas, 20.2 C_1–C_4, and 75.6 C_3+ hydrocarbons.

Less active were samples of 6–8 mesh granules of American synthetic-ammonia-type catalysts, as exemplified by one whose composition was 100Fe:6.92MgO:1.12Cr_2O_3:0.93SiO_2:0.91K_2O. In a 5-week test at 7 atm in the U. S. Bureau of Mines laboratory, the average temperature was 256.0°C for 70 per cent conversion per pass and the yield 14.2 g CH_4 per cu m of feed gas, 47.5 C_1–C_4, and 94.4 C_3+ hydrocarbons. The synthesis temperature and gaseous hydrocarbon yields were higher than those obtained from the previous catalysts. In addition, the catalytic activity showed a steady decrease during the test, whereas the synol and cemented catalysts increased in activity. The activity of this fused catalyst was improved in two ways. When 40–60 mesh granules were tested, the average temperature in a 7-week test was 226.6°C for 70 per cent conversion per pass and the product distribution was as follows, in grams per cubic meter of feed gas: 8.0 CH_4, 30.4 C_1–C_4, and 98.4 C_3+ hydrocarbons. When the test was made with nitrided 6–8 mesh granules, the following data were obtained in a 7-week test at 7 atm: temperature,

240°C for 70 per cent conversion per pass; yield, 13.6 g CH_4 per cu m of feed gas, 41.5 C_1–C_4, and 88.9 C_3+ hydrocarbons. These values include oxygenated compounds dissolved in the hydrocarbon phases; the alcohol content of the <185°C fraction was larger in tests with nitrided catalysts than under similar conditions with reduced catalysts.

Comparison can be made of various types of iron catalysts on the basis of mechanical strength and resistance to spalling. A finely powdered magnetite catalyst cemented with ball clay retained its mechanical strength after reduction; however, its activity decreased rapidly during synthesis in a U. S. Bureau of Mines catalyst-testing unit. The synthetic-ammonia-type catalysts were very hard in their original state, but when reduced retained only one-half their mechanical strength. The cemented catalysts containing borax and alumina retained only 0.1, and the sintered, alkalized glomerule catalyst (for description see Chapter 3, p 282) only 0.01 of the original mechanical strength after reduction. Precipitated catalysts disintegrated upon pretreatment.

In a U. S. Bureau of Mines dry-bed, catalyst-testing unit, the alkalized glomerules, whose composition was 100Fe:0.6K_2O, maintained an average temperature of 220.1°C for a 70 per cent conversion per pass in a 10-week test at 7 atm and produced 7.6 g CH_4 per cu m of feed gas, 27.1 C_1–C_4, and 112.8 C_3+. Such a catalyst would probably be satisfactory in the slurry process but not in the oil-circulation process, in which a rigid granule is required. For the oil-circulation process a good cemented or fused catalyst would be suitable. In fluidized systems, synthetic-ammonia-type and alkalized iron oxide powder catalysts have been used. However, carbon deposition and wax accumulation, resulting in defluidization, have been observed with these catalysts. To avoid these difficulties, a hard, nitrided catalyst may be useful.

The third criterion suggested for evaluating catalysts is the important factor of relative manufacturing costs. Because of the expensive nature of precipitated and fused synthetic-ammonia-type catalysts, work is in progress in the laboratories of the U. S. Bureau of Mines and the various oil companies on the use of readily available iron ores and industrial by-product iron oxides for catalyst manufacture. The U. S. Bureau of Mines has, for example, prepared adequately active cemented (with Al_2O_3) catalysts starting with finely divided magnetite ore concentrated by magnetic separation, pigment-grade iron oxide, mill scale from the steel industry, and goethite ore. Catalysts so prepared were found to be more active than the fused synthetic-ammonia type but were not sufficiently resistant to mechanical disintegration. Other inexpensive iron powders may be used to prepare active catalysts provided that they do not contain a constituent such as sulfur, which is a catalyst poison in the Fischer-Tropsch synthesis.

CHAPTER

4

Characteristics of the Synthesis of Importanee in Proeess Development

TEMPERATURE AND PRESSURE COEFFICIENTS; CATALYST DURABILITY

The hydrogenation of carbon monoxide to produce chiefly straight-chain paraffin hydrocarbons and water or carbon dioxide or both is a heterogeneous reaction requiring carefully prepared nickel, cobalt, iron, or ruthenium catalysts and purified synthesis gas containing less than 0.2 g of sulfur in 100 cu m. Branched-chain hydrocarbons, aromatic hydrocarbons, aliphatic alcohols, aldehydes, and acids also are produced in amounts varying with the type of catalyst and the operating conditions. The heat liberated by the reaction is large, namely, 7,200 Btu per lb of oil product. The optimum temperature ranges are 170°–205°C for nickel and cobalt, 200°–325°C for iron, and 160°–225°C for ruthenium. This combination of a highly exothermic reaction with a relatively narrow range of optimum operating temperature makes the problem of removal of the heat of reaction most important in the design of the process and its equipment.

Nickel catalysts cannot be successfully used at pressures much above atmospheric because of excessive corrosion due to nickel carbonyl formation. Cobalt and iron catalysts may be used up to about 20 atm before appreciable corrosion by carbonyl formation occurs. Ruthenium is only slightly active at atmospheric pressure; 100 atm pressure is necessary for a space-time-yield of the order of that obtained for the other catalysts at pressures in the range 1–20 atm. All the catalysts yield detectable amounts of metal carbonyls at optimum reaction temperatures and pressures. Pichler [1] thinks that this fact is important for discussions of the probable mechanism of the reaction.

[1] H. Pichler, Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen, *U. S. Bur. Mines Spec. Rept.*, 1947. Translation reproduced in T.O.M. Reel 259, Frames 467–654.

The temperature coefficients for the rate of the synthesis on nickel [2] and cobalt [3] have been measured; they are in the range 1.6–1.8 per 10°C increase in temperature. The pressure coefficient of the synthesis rate is defined as n in the equation:

$$\text{rate} = Ae^{-\Delta E/RT}p^n$$

where A and R are constants, e is the base of natural logarithms, ΔE is the activation energy, T is the absolute temperature, and p is the partial pressure of synthesis gas. For cobalt catalysts, n is close to zero when measured in the presence of appreciable concentrations of the reaction products.[4] When the concentration of reaction products is kept very low by using high space velocities and very low conversions per pass over cobalt catalysts, n is about 0.5.[5] For iron catalysts in the presence of synthesis products n is about 1.0.[1] The activation energy ΔE is in the range 20–26 kcal for cobalt and iron catalysts.

The durability of cobalt [6] and iron [7] catalysts is much greater at 7–20 atm pressure than at atmospheric pressure. Some of the data on the change in catalyst durability with pressure are graphically presented in Figure 1 for a cobalt catalyst and in Figure 2 for an iron catalyst. The pressures given in Figure 1 are gauge readings, whereas those in Figure 2 are absolute pressures. The durability of both cobalt and iron catalysts at atmospheric pressure can be greatly extended by periodic extraction with a solvent or by flushing with hydrogen at frequent intervals. Both procedures remove large (20–100 per cent of the catalyst weight) amounts of wax and high-boiling oxygenated compounds. The marked increase in durability at intermediate pressures of 7–20 atm probably is due to the formation of liquid oil films of relatively low-molecular-weight hydrocarbons on the catalyst surfaces. Such liquid oil would dissolve wax and high-boiling oxygenated compounds from the pores of the catalyst granules and thereby provide a continuous extraction and consequent regeneration of the catalyst activity. The markedly lower durability at pressures above 30 atm may be due to corrosion of the catalyst surfaces by carbonyl formation.

[2] A. Aicher, W. W. Myddleton, and J. J. Walker, *J. Soc. Chem. Ind. London*, **54**, 313–20T (1935).

[3] R. B. Anderson, A. Krieg, B. Seligman, and W. E. O'Neill, *Ind. Eng. Chem.*, **39**, 1,548–54 (1947).

[4] R. B. Anderson, A. Krieg, R. A. Friedel, and L. S. Mason, *ibid.*, **41**, 2,189–97 (1949).

[5] S. Weller, *J. Am. Chem. Soc.*, **69**, 2,432–6 (1947).

[6] F. Fischer and H. Pichler, *Brennstoff-Chem.*, **20**, 41–8 (1939).

[7] T.O.M. Reel 101, Document PG-21,559-NID, Report on the Middle-Pressure Synthesis with Iron Catalysts, June 1940.

The curves of Figure 1 are not isothermal. Increasing time of operation was associated with gradual lowering of the activity of the catalyst.

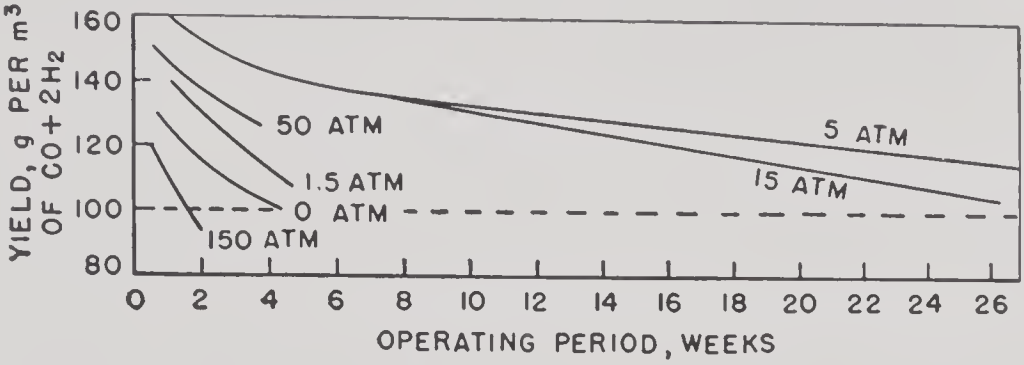


FIGURE 4–1. Variation of yield with time at various pressures. Reproduced from reference 6.

This reduction could be partly compensated by raising the reaction temperature. In the experiments at 5–15 atm, the initial temperatures of 175°–180°C were not raised to 195°C even after 6 months of operation.

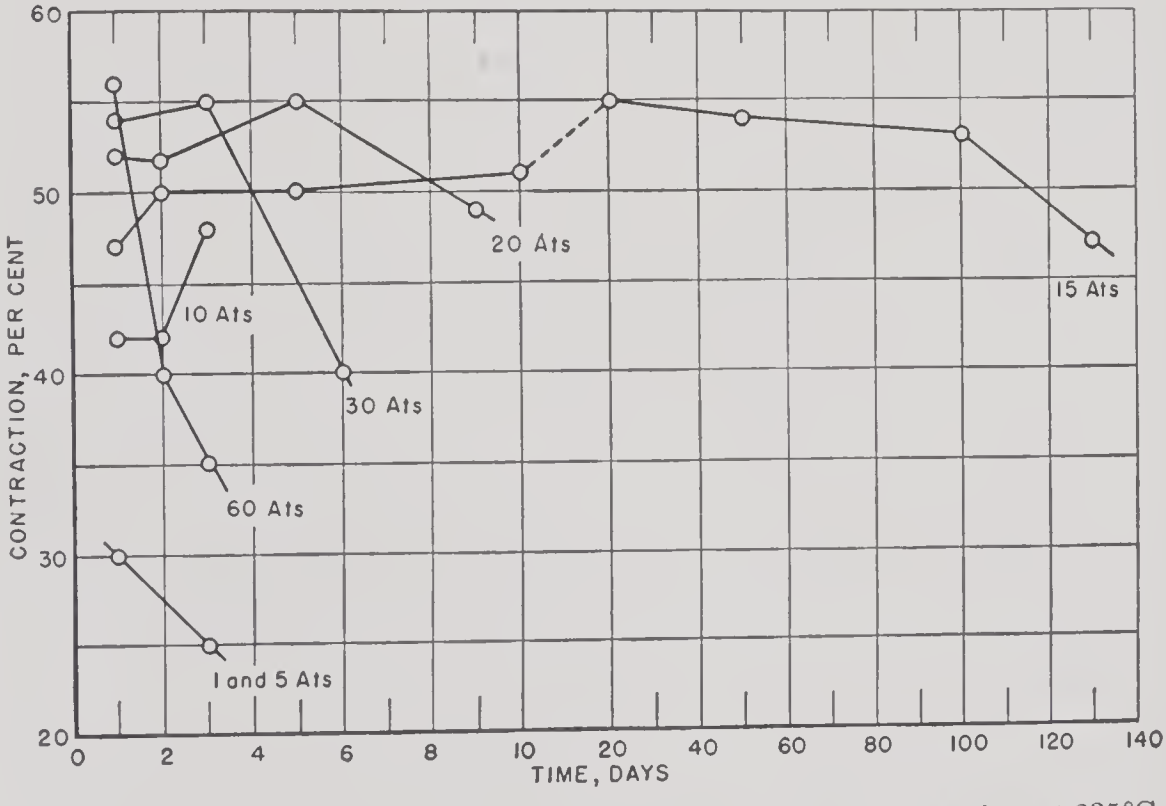


FIGURE 4–2. Effect of pressure on durability of a precipitated iron catalyst at 235°C, using $3CO + 2H_2$ synthesis gas.

At 1 atm, the initial temperature of 180°C had to be increased to 195°C, after only 5 weeks of operation. The contractions shown in Figure 2, for an iron catalyst, may be related to degree of conversion of carbon monoxide as follows: As the usage ratio of carbon monoxide to hydrogen

was about 1.5 to 1, about 88 per cent of the carbon monoxide reacted according to the equation:

$$2nCO + nH_2 = (CH_2)_n + nCO_2$$

and about 12 per cent according to the equation:

$$nCO + 2nH_2 = (CH_2)_n + nH_2O$$

On this basis, it is calculated that a contraction of 50 per cent corresponds to about 70 per cent conversion of the carbon monoxide.

PRODUCT DISTRIBUTION AT DIFFERENT PRESSURES

Table 1 contains data obtained by Fischer and Pichler [6] on the change in the boiling range of the product with pressure. As the pressure was increased above atmospheric, the total yield of hydrocarbon at first increased and then (at about 15 atm) decreased. A cobalt-thoria-kieselguhr catalyst and a constant throughput of 1 l (measured at atmospheric pressure) per hr of $2H_2 + 1CO$ gas per g of cobalt metal were used. The data are averages for 4-week operation. Only a single pass of the gas through the catalyst was made, and there was no catalyst regeneration.

Table 1. Product Distribution at Different Pressures for a Cobalt Catalyst

Pressure, atm	Yields, g per cu m of synthesis gas ($2H_2 + 1CO$)				
	Total Solid and Liquid Hydrocarbons	Paraffin Wax	Oil Boiling above 200°C	Gasoline Boiling below 200°C	Gaseous Hydrocarbons, C_1–C_4
1.0	117	10	38	69	38
2.5	131	15	43	73	50
6.0	150	60	51	39	33
16.0	145	70	36	39	33
51.0	138	54	37	47	21
151.0	104	27	34	43	31

The throughput was held constant, and therefore the contact time increased in direct proportion to the pressure. The yield of all hydrocarbons (column 2 plus column 6) increased from 155 per cu m at atmospheric pressure to 181 at 2.5 and 183 at 6 atm, and then decreased with

further pressure increase. As the theoretical yield was about 208 g per cu m, the maximum percentage of conversion to hydrocarbons was about 88. The rapid decrease in yield of hydrocarbons for pressures above about 16 atm was probably due to corrosion of active catalyst surface by carbonyl formation and by the stronger adsorption of the oxygenated organic compounds which were produced in larger amounts at the higher pressures.

Similar data were graphically presented by Martin,[8] whose curves are reproduced in Figure 3. These curves show that a maximum percentage

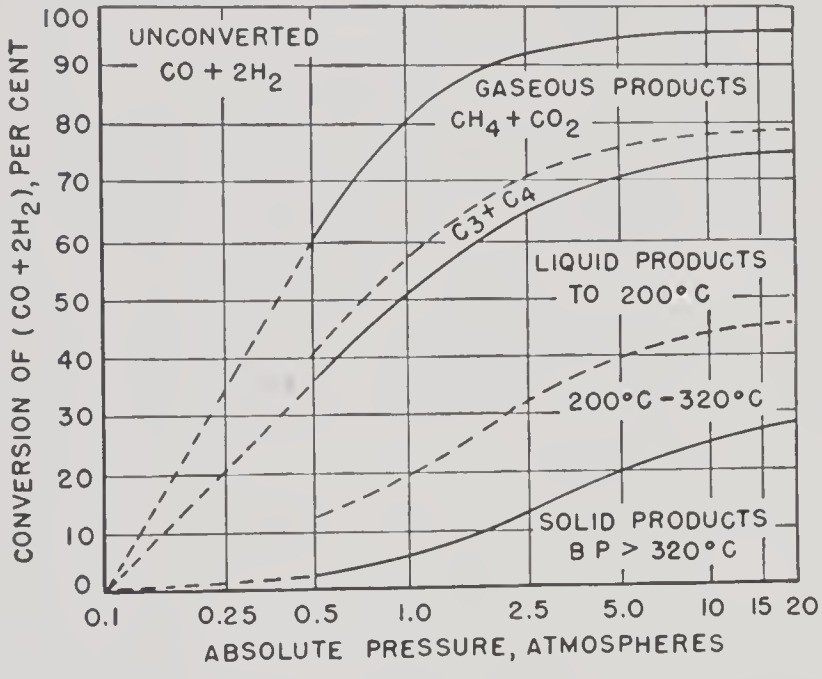


FIGURE 4–3. Effect of pressure on total yield and yield of various fractions. Constructed from data in second paper of reference 8.

of conversion is attained at about 10 atm pressure. The data of Table 1 and the curves of Figure 3 are not isothermal, for the temperature was adjusted in the range 175°–200°C for each test so as to obtain maximum conversion to liquid product.

A more detailed characterization of the products from a cobalt catalyst at 1 and 7 atm pressure was presented in Table 10 in Chapter 3. In addition to the marked increase in wax production already shown in Table 1, Table 10 in Chapter 3 shows that the products at 7 atm are more saturated than those at 1 atm pressure.

Additional data on the changes with pressure in the boiling range of the normally liquid products from a cobalt-thoria-magnesia-kieselguhr catalyst (100:5:7.5:200 parts by weight) were obtained by the Ruhr-

[8] F. Martin, *Ind. Chemist*, **13**, 320–6 (1937); *Oel, Kohle, Teer*, **13**, 691–7 (1937); *Chem. Fabrik*, **12**, 233–40 (1939).

chemie [9,10] and are presented in Tables 2 and 3. The data of Table 2 show that the molecular weight of the liquid products increases with increasing operating pressure. The more detailed data on the effect of pressure, presented in Table 3, show that at about 3 atm there is a definite increase in the weight per cent of product boiling above 320°C, and an increase in the per cent of carbon monoxide converted to oil. Possibly this is the "dew-point" of the reaction mixture at about 190°C, so

TABLE 2. BOILING RANGES OF LIQUID PRODUCTS FROM A COBALT CATALYST AT DIFFERENT PRESSURES

Operating Pressure, atm	Cumulative Volume Per Cent Distilling to				
	100°C	150°C	200°C	250°C	300°C
5	22	33	51	62	73
7	15	28	41	53	64
10	14	26	38	49	61

that a substantial film of liquid hydrocarbons is formed at pressures of about 3 atm. Such a film would increase the contact time of the liquid products with the catalyst. From 3 to 7 atm there is little change in CO conversion or product distribution.

At an operating pressure of 1 atm and at about 230°C, the product from iron catalysts contains much more wax than that from cobalt catalysts. Thus the weight per cent of the product boiling above 320°C is 11 per cent for cobalt and 20 per cent for iron.[10,11] At about 10 atm operating pressure, the corresponding figures are 30 for cobalt and 60 for iron (at about 230°C operating temperature).[11,12] Roelen [12] presents a table showing the effect of operating pressure on product distribution for an iron catalyst but does not state the composition of the catalyst and the operating conditions. The catalyst probably was a precipitated one promoted with copper, calcium oxide, and potassium carbonate, which Roelen usually reduced with hydrogen at 300°–325°C and operated at

[9] T.O.M. Reel 33, Bag 3,440, Target 30/5.01, Item 24.

[10] T.O.M. Reel 36, Bag 3,451, Item 13.

[11] C. C. Hall, S. R. Craxford, and D. Gall, Interrogation of Dr. Otto Roelen of Ruhrchemie A.G., B.I.O.S. Target 30/5.01, PB 77,705 (1946).

[12] O. Roelen, Ueber die Kohlenwasserstoff-Synthese mittels Eisenkatalysatoren, T.O.M. Reel 33, Bag 3,440, C.I.O.S. Target 30/5.01, Item 6.

TABLE 3. EFFECT OF DIFFERENT OPERATING PRESSURES ON SYNTHESIS, USING A Co-ThO_2-MgO-KIESELGUHR CATALYST IN A PILOT-PLANT, DOUBLE-TUBE REACTOR CONTAINING 5 L OF CATALYST

Pressure, atm, absolute	0.2		1.0		2.0		3.0		4.0		5.0		6.0		7.0	
Duration of test, hr	6		3		11		11		11		18		7		8	
Space velocity per hr [a]	107		111		113		111		108		109		106		110	
Temperature, °C	190.7		190.7		191.8		187.3		187.6		187.5		192		196	
Gas analyses, volume per cent																
A. Feed. *B*. Off gas	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
CO_2	14.1	35.3	13.8	31.0	13.9	34.2	13.7	34.2	13.6	34.9	13.9	34.3	14.3	35.1	14.3	35.4
C_nH_m	....	1.1	....	1.1	....	0.7	....	0.2	....	0.6	....	0.4	....	0.3	....	0.2
CO	28.2	18.8	27.9	20.3	28.0	19.1	28.2	20.5	28.5	20.0	28.3	20.4	27.7	19.6	27.7	18.9
H_2	54.2	29.3	54.4	32.2	54.0	27.3	54.2	29.8	53.3	27.0	53.5	28.9	53.8	29.0	53.9	28.6
CH_4	....	8.3	....	8.5	....	10.3	....	7.8	....	7.8	....	7.3	....	7.8	....	8.7
N_2	....	7.1	....	6.8	....	8.3	....	7.3	....	9.6	....	8.6	....	8.1	....	8.1
Carbon number	....	1.10	....	1.07	....	1.00	....	1.00	....	1.00	....	1.00	....	1.08	....	1.11
Contraction, per cent	60		55.5		58.6		58.5		59.6		58.8		58.6		58.7	
Per cent of CO entering																
Total converted	76.6		69.5		74.4		72.7		76.4		74.2		72.6		73.7	
To oil	59.7		50.7		56.3		59.0		61.4		61.8		58.8		57.4	
To CH_4 + gasol	16.9		18.8		17.5		11.8		13.0		11.5		12.7		14.2	
To CO_2	....		....		....		1.8		2.0		0.9		0.9		1.8	
Per cent of CO converted																
To oil	77.9		73.0		76.5		81.3		80.4		83.3		81.1		78.0	
To CH_4 + gasol	22.1		27.0		23.5		16.2		17.0		15.5		17.6		19.4	
To CO_2	....		.....		.....		2.5		2.6		1.2		1.3		2.6	
Use ratio, H_2:CO	2.05		2.12		2.12		2.13		2.08		2.09		2.14		2.11	
Oil, g per cu m of $2H_2 + 1CO$	.....		107		119		125		128		128		125		120	
Specific gravity of oil product at 15°C	0.727		0.718		0.733		0.740		0.747		0.743		0.743		0.734	
Boiling range of oil product, cumulative weight per cent to																
100°C	19.5		26.2		23.2		22.0		21.0		22.7		21.5		24.9	
200°C	59.4		63.0		56.2		49.8		49.9		51.4		50.7		55.4	
300°C	85.5		88.2		80.4		75.3		74.0		74.5		74.2		78.3	
320°C	89.0		91.3		84.1		78.8		77.6		78.4		77.8		81.8	
360°C	95.5		96.7		90.5		85.2		84.8		85.8		85.4		90.0	
Weight per cent above 320	11.0		8.7		15.9		21.2		22.4		21.6		22.2		18.2	

[a] Volumes of synthesis gas (at atmospheric pressure and 20°C) per volume of catalyst per hour.

230°–245°C. Roelen's data [12] are reproduced in Table 4. Comparisons should be made at constant conversion, and therefore the data at 1 and 5 atm should not be included. Inspection of the data at 3, 10, and 20 atm shows an increase in wax and corresponding decrease in gasoline and Diesel oil production with increasing pressure. The olefin contents

Table 4. Change in Product Distribution with Pressure for Operation with Water Gas ($1H_2$:1CO), Using a Precipitated Iron Catalyst

Pressure, atm, absolute	1	3	5	10	20
Conversion of carbon monoxide, per cent	95	75	70	75	75
Specific yield of C_3+, g per cu m of feed gas	90	98	86	118	120
Weight per cent in liquid product					
Gasoline	57	32	30	25	22
Diesel oil	24	30	25	20	22
Wax	19	38	45	55	56
Volume per cent of olefins in					
Gasoline	68	64	63	62	63
Diesel oil	41	48	49	47	46

of the gasoline and Diesel oil fractions do not change much with increasing pressure, in contrast to the decreasing unsaturation at higher pressures for cobalt catalysts (see Table 10, Chapter 3).

EFFECT OF NITROGEN, METHANE, CARBON DIOXIDE, AND OLEFINS IN FEED GAS

The effect of dilution with nitrogen is best illustrated by some of the experimental data of Hall and Smith,[13] the results of which are presented in Table 5. For comparison with the results of test periods 26–27 in which synthesis gas containing 35 per cent of nitrogen was used, those of test periods 23–29 and 21–22 using synthesis gas, with only 4 per cent nitrogen, are included in Table 5. It is apparent that an increase in space velocity alone results in a decreased yield; thus, test period 23–29 at 93.5 space velocity and 21–22 at 131 space velocity yielded, respectively, 142 and 113 g of liquids plus solids per cu m of $2H_2 + 1CO$. At about the same space velocity of feed gas (compare test period 26–27 with 21–22), substitution of about 30 per cent of the $2H_2 + 1CO$ by nitrogen results in a somewhat higher yield of liquids plus solids per cubic meter of $2H_2 + 1CO$. The distributions of the liquid plus solid product in test periods

[13] C. C. Hall and S. L. Smith, *J. Inst. Petroleum*, **33**, 439–59 (1947).

TABLE 5. EFFECT OF NITROGEN DILUTION

(Laboratory experiments with 100 cc of 100Co:6ThO_2:3MgO:250 kieselguhr catalyst containing 9.35 g of cobalt; operating pressure 10 atm.)

Test Period	Temperature, °C	Feed-Gas Composition, volume per cent				Liters of $2H_2 + 1CO$ per g of Cobalt per hr	Space Velocity, volumes of feed gas per volume of catalyst per hr	Yield of Liquids + Solids, g per cu m of		Boiling Range, per cent by weight of liquids + solids			
		CO_2	CO	H_2	N_2			Feed Gas	$2H_2 + 1CO$	To 150	150–200	200–300	>300
23–29	192.5	2.5	31.5	62.0	4.0	1.0	93.5	133	142	24.6	12.8	22.6	40.0
26–27	193	3.1	20.0	41.8	35.1	1.0	138	112	120	36.7	14.8	21.2	27.3
21–22	192	2.5	31.5	62.0	4.0	1.40	131	106	113	33.3	14.8	28.8	23.1

26–27 and 21–22 are quite similar, despite the dilution with nitrogen in test period 26–27, whereas that of test period 23–29 at the lower space velocity is considerably different from those at the higher space velocity.

Similar although less precise results on the effect of nitrogen dilution were obtained by Storch and his coworkers [14] and are presented in Table 6. The last column of this table contains the "corrected" yield of liquids

Table 6. Effect of Nitrogen Dilution

(Laboratory experiments with 50 cc of 100Co:6ThO_2:12MgO:200 Hyflo-Super-Cel; operating pressure, 1 atm.)

Test No.	Temperature, °C	Feed-Gas Composition, volume per cent				Space Velocity, volumes of feed gas per volume of catalyst per hr	Yield of Liquids + Solids, g per cu m		
		CH_4	CO	H_2	N_2		Feed Gas	$2H_2 + 1CO$	$2H_2 + 1CO$ Corrected [a]
69f	193	0.3	30.0	68.7	1.0	102	89.2	90.4	92.3
70g	188	0.3	30.0	68.7	1.0	80	108	109	87.2
71b	185	0.3	30.0	68.7	1.0	83	93.3	95	78.8
71c	193	0.3	30.0	68.7	1.0	84	109	110	92.4
69b	186	1.3	24.2	58.2	16.3	94	89.6	107	100.6
69d	193	1.3	24.2	58.2	16.3	91	106	127	115.6
69g	193	0.2	27.8	57.2	16.3	94	98.8	118	111.0
70b	187	0.1	26.7	44.4	28.8	129	112.8	158	204.0
70c	188	0.1	26.7	44.4	28.8	129	75.8	105	135.4
70d	193	0.1	26.7	44.4	28.8	133	87.8	123	163.5
70e	196	0.1	26.7	44.4	28.8	130	84.9	119	154.6

[a] Grams per cubic meter of $2H_2 + 1CO \times \frac{\text{space velocity}}{100}$.

plus solids in grams per cubic meter of $2H_2 + 1CO$. It is calculated from the next to the last column by assuming that the yield per cubic meter is inversely proportional to the space velocity in the range 90–135. The average "corrected" yield for the synthesis gas containing 1.0 per cent of nitrogen is 88, for the 16.3 per cent nitrogen gas 109, and for the 28.6 per cent nitrogen gas 163 g per cu m. The "corrected" yield is only an approximation, and the lower ratio of hydrogen to carbon monoxide in the 28.6 per cent nitrogen tests makes the comparisons quantitatively uncertain. Both the "corrected" and uncorrected data of Table 6 indicate, however, the same trend as was observed in Table 5, namely, that at the same space velocity replacement of 16–30 per cent of the hydrogen plus carbon monoxide by nitrogen results in an appreciably larger yield of liquids plus solids per cubic meter of $2H_2 + 1CO$. The

[14] H. H. Storch, R. B. Anderson, L. J. E. Hofer, C. O. Hawk, H. C. Anderson, and N. Golumbic, *U. S. Bur. Mines Tech. Paper* 709 (1948), 213 pp.

volume of carbon monoxide converted per volume of catalyst per hour decreases, however, with increasing inert content at constant feed-gas space velocity.

This decrease in space-time conversion of carbon monoxide with increasing inert content at constant feed-gas space velocity is illustrated by the data in the last two rows of Table 7. The data of this table were obtained by the Ruhrchemie [15] in a pilot-plant operation in 1941. Comparison of the oil yield for the first three columns of Table 7 shows that, for 21.2, 41.6, and 50.8 per cent of inerts in the feed gas, this yield was 90.5, 107.5, and 115.4 g per cu m of $CO + H_2$. This extends the conclusions from the data of Tables 5 and 6, namely, that at constant space velocity of feed gas substitution of nitrogen for $CO + H_2$ results in an increased yield per cubic meter of $CO + H_2$, to cases where mixtures of nitrogen, methane, and carbon dioxide are substituted for $CO + H_2$. This increase in yield of oil per cubic meter of $CO + H_2$ is not sufficient, however, to compensate for the decrease in volume of $CO + H_2$ flowing through unit volume of the catalyst per unit time. Thus, as is shown by comparison of the data in the last two rows of the first three columns of Table 7, the space-time conversion of $CO + 2H_2$ decreases with increasing content of inerts. The data in the remaining five columns of Table 7 show that, with 40–50 per cent of inerts, the specific yield, grams of oil per cubic meter of $CO + 2H_2$, is uniformly higher than that of the third column with 20 per cent of inerts, and that conversely the space-time conversion of $CO + 2H_2$ is lower for the higher inert content.

In the Ruhrchemie documents,[15,16] there are also data which show that the product distribution as indicated by distillation is, at constant space velocity of feed gas, unchanged by dilution of $CO + 2H_2$ with carbon dioxide, and mixtures of carbon dioxide and nitrogen. (See also Table 5.)

The volumes of methane produced per 100 volumes of $CO + 2H_2$ in the feed gas of the 13–51, 52–67, and 71–80 days' operating periods of Table 7 are calculated to be 3.35, 2.78, and 2.46, respectively. As the corresponding methane concentrations in the feed gas were 6.9, 4.2, and 0.4 per cent, there appears to be a small increase in methane produced with increasing methane in the feed. This conclusion is in conflict with recent results obtained by Craxford [17] and by Prettre and his coworkers.[18] Craxford's data [17] indicate that methane when present to the extent of about 50 per cent of the synthesis gas participates in the Fischer-Tropsch reaction on a cobalt catalyst. Prettre's data [18] indicates that a much

[15] T.O.M. Reel 37, Bag 3,451, Item 14.
[16] T.O.M. Reel 1, Bag 2,168, Item 17.
[17] S. R. Craxford, *Fuel*, **26**, 119–23 (1947).
[18] M. Prettre, C. Eichner, and M. Perrin, *Compt. rend.*, **224**, 278–9 (1947).

TABLE 7. EFFECT OF "INERTS" (NITROGEN, CARBON DIOXIDE, AND METHANE) ON SYNTHESIS, USING A Co-ThO_2-MgO-KIESELGUHR CATALYST IN A PILOT-PLANT CONTAINING 206 L OF CATALYST, AND OPERATING AT 7 ATM PRESSURE

"Inerts," volume per cent in feed gas	50.8		41.6		21.2		40.4		40.0		40.6		50.3		50.0	
Operating time, days	13–51		52–67		71–80		93–100		101–125		128–143 175–188		144–174		189–205	
Space velocity per hr [a]	99		101		99		97		78		81		97		100	
Temperature, °C	174.5		176.5		176.5		179		179		182		182		188.5	
Gas analyses, volume per cent																
A. Feed. *B*. Off gas	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
CO_2	28.0	42.5	23.0	37.1	13.6	24.2	19.3	31.6	18.1	30.8	20.1	36.2	26.3	39.5	26.2	40.2
C_nH_m	0.3	0.2	0.1	0.2	....	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.2	0.1	0.1	0.1
CO	17.0	8.5	19.8	11.5	26.1	20.7	19.9	11.7	20.6	10.6	19.7	8.8	16.6	8.7	16.9	8.3
H_2	32.2	12.9	38.6	19.4	52.7	36.9	39.7	19.5	39.4	17.5	39.7	15.9	33.1	14.4	33.1	13.5
CH_4	6.9	12.2	4.2	9.1	0.4	4.3	4.1	9.7	5.1	11.9	4.5	11.0	5.5	10.1	5.5	10.5
N_2	15.5	23.6	14.2	22.6	7.2	13.5	16.8	27.2	16.9	28.9	15.9	27.8	18.2	27.1	18.2	27.3
Contraction, per cent	33		35.9		45.7		39.6		41.2		43.6		34.0		35.3	
Use ratio, H_2:CO	2.08		2.11		2.19		2.18		2.08		2.09		2.14		2.12	
Conversion, per cent by volume of																
CO	66.5		62.6		57.1		64.3		69.3		74.6		65.7		68.0	
H_2	73.2		67.9		62.0		70.3		73.9		77.4		71.0		73.7	
$CO + 2H_2$	71.0		67.4		60.4		68.3		72.3		76.5		69.2		71.8	
Volume per cent converted to oil																
CO	79.6		80.1		75.8		71.4		68.2		74.3		75.4		69.3	
$CO + 2H_2$	51.6		51.5		47.5		44.9		44.2		48.2		48.0		44.4	
Oil yield per cu m of $CO + 2H_2$	115.4		107.5		90.5		96.7		101.0		116.0		105.1		100.5	
Liters of $CO + 2H_2$ in feed per l of catalyst per hr	48.7		59.0		78.0		57.7		45.6		48.3		47.9		50.0	
Liters of $CO + 2H_2$ converted per l of catalyst per hr	34.6		39.8		47.1		39.4		33.6		36.9		33.2		35.9	

[a] Volumes of synthesis gas (at atmospheric pressure and 20°C) per volume of catalyst per hour.

higher methane content of about 90 per cent of the synthesis gas and special catalysts are essential for the participation of methane in the reaction. The work of both experimenters should be repeated with careful attention to the accuracy of the gas analyses and to mass balances.

Data for methane production in Ruhrchemie commercial-size plants are given in Table 8 [19] for operation at 1 atm and in Table 9 [20] for operation at 7 atm pressure. The methane produced as per cent of the carbon

Table 8. Methane Production, Average of Data for 1 Year (1943), of Ruhrchemie Commercial Two-Stage Operation with Cobalt-Thoria-Magnesia-Kieselguhr Catalyst at 1 atm Pressure

	Methane, volume per cent in feed gas	Methane Produced, volume per cent of CO in feed to each stage	Methane Produced, g per cu m of $CO + 2H_2$ in total gas fed to plant
First stage	4.9	15.1	15.1
Second stage	15.3	16.4	6.5

Table 9. Methane Production, Averages of Ruhrchemie Commercial Three-Stage Operation with Cobalt-Thoria-Magnesia-Kieselguhr Catalyst at 7 atm Pressure for November to February 1944

Stage Number	1	2	3
Temperature, °C	198.9	196.4	196.4
CH_4, volume per cent in the feed gas to each stage	0.4	4.2	9.2
CH_4 produced, volume per cent of CO in feed to each stage	11.9	13.2	17.9
CH_4 produced, g per cu m of $CO + 2H_2$ in total gas fed to plant	13.8	5.4	2.0

monoxide converted in each stage increases somewhat with increasing methane content of the feed, as was the case for the data of Table 7. The number of grams of methane per cubic meter of $CO + 2H_2$ in the total gas fed to the plant, however, decreases sharply in the second and third stages. No consumption of methane is indicated by the Ruhrchemie data.

A study of the effect of the addition of gasol ($C_3 + C_4$ product of Ruhrchemie Fischer-Tropsch process) and of pure propylene and butylene to $2H_2 + 1CO$ synthesis gas was the subject of a dissertation [21] by

[19] T.O.M. Reel 44, Bag 3,441, Item 24.
[20] T.O.M. Reel 44, Bag 3,441, Item 20.
[21] F.I.A.T. Reel 115X, Frames 700–803.

E. Ruschenburg at the Technischen Hochschule in Dresden. The experiments were done at 1 atm pressure in laboratory reactors containing about 40 g of Ruhrchemie cobalt catalyst. The gasol used contained, in volume per cent, 11.9 propylene, 23.0 butylene, 37.1 propane, 21.5 butane, and 6.5 total of nitrogen, ethylene, ethane, carbon monoxide, and carbon dioxide. Table 10 contains the results, showing the change in olefin conversion with partial pressure of olefin in the feed gas. Ex-

Table 10. Conversion of Olefins Added to $2H_2 + 1CO$ Synthesis Gas on Ruhrchemie Cobalt Catalyst

Experiment No.	Per Cent Gasol in Synthesis Gas	Space Velocity [a]	Temperature, °C	Catalyst Age, hr	Per Cent Olefins in Synthesis Gas	Per Cent Conversion of Olefins	Per Cent Conversion × Per Cent Olefins $^{0.5}$	Per Cent of Normal Amount of Water Produced
1	50.0	4.0	187	328–470	17.5	15.4	64	33
2	14.3	2.3	187	328–470	5.0	38.0	85	71
3	4.4	3.8	188	300–400	1.5	65.5	80	94
4	4.7	3.7	190	294–408	1.7	65.7	86	100
5	6.1	3.7	190	294–408	2.1	63.8	92	98
6	5.7	3.9	192	500–600	2.0	46.1	65	..
7	7.8	3.6	200	750–870	2.7	85.6	140	..
8	5.5	10.2	188	147–260	1.7	44.1	58	..
9	7.3	11.0	191	700–750	2.5	43.5	69	..
10	12.2	11.5	190	321–413	4.3	34.0	71	91
11	12.2	11.1	190	321–413	4.3	40.6	84	93
12	5.3	1.9	191	300–475	1.8	73.0	98	100
				Pure propylene				
13		4.2	187	350–400	5.6	11.2	26	..
14		4.1	187	350–400	6.0	2.7	7	..
15		3.9	188	450–500	7.5	9.1	25	..
16		3.5	188	450–500	7.3	4.0	11	..
17		4.1	190	670–800	3.5	10.0	19	..
18		3.9	190	670–800	3.0	23.6	41	..
				Pure butylene				
19		12.0	...	...	0.8	100.0	90	..
20		24.0	189	200	2.2	63.0	93	..

[a] Liters of $2H_2 + 1CO$ + gasol (or pure olefins) per hour passed over 40 g (about 110 cc) of Ruhrchemie cobalt catalyst.

periments 1–5 and 10–12, inclusive, were done with catalyst aged 300–500 operating hr in the temperature range 187°–191°C, and the results probably are comparable within the limits of reproducibility of such

tests. The results of these experiments show that the percentage conversion of the olefins in the gasol is essentially independent of the hourly space velocity and inversely proportional to about the square root of the olefin concentration. Experiments 13–18, inclusive, with pure propylene, when compared with those for gasol (experiments 5 and 10–12) and for pure butylene (experiments 19 and 20), show that the degree of conversion under comparable conditions was five- to ten-fold lower for propylene. Included in Table 10 are some data on the ratio of the amount of water produced when gasol was present in the synthesis gas to the amount formed when no gasol was present. It appears that in the range 4–50 per cent gasol the water produced was 100–33 per cent of that produced when no gasol was present. A corresponding but inverse variation in carbon dioxide production occurred.

It appears that olefins retard the synthesis and accelerate the water-gas shift reaction. More precise experiments are needed, however, before any firm conclusions can be drawn.

Processes Using Fixed Beds of Granular or Pelleted Catalysts and Cooling by Indirect Heat Exchange

THE RUHRCHEMIE PROCESS

In 1927–1932, Fischer and his coworkers [22–24] developed more active promoted nickel and cobalt catalysts and increased the yield per pass to more than 100 g of oil per cu m of $2H_2 + 1CO$. In 1932–1934, Fischer and his coworkers [25–29] were engaged in process development work, using a Ni-MnO-Al_2O_3-kieselguhr catalyst. Because of the highly exothermic character of the reaction, Fischer found it essential that the path of heat transfer from a granule of catalyst to a cooling surface be less than 10 mm, preferably about 7 mm. His first experimental plant consisted of a battery of cells 12 mm thick by 1.2 m wide by 5 m high, immersed in an oil bath. A yield of 70 g of oil per cu m of $2H_2 + 1CO$ was obtained at 190°–210°C and at atmospheric pressure. In 1934, the

[22] F. Fischer, *Brennstoff-Chem.*, **11,** 489–500 (1930).
[23] F. Fischer and K. Meyer, *ibid.*, **12,** 225–8 (1931).
[24] F. Fischer and H. Koch, *ibid.*, **13,** 61–8 (1932).
[25] F. Fischer, H. Pichler, and R. Reder, *ibid.*, **13,** 421–8 (1932).
[26] F. Fischer, O. Roelen, and W. Feisst, *ibid.*, **13,** 461–8 (1932).
[27] R. Hartner-Seberich and H. Koch, *ibid.*, **13,** 308–10 (1932).
[28] F. Fischer and H. Koch, *ibid.*, **13,** 428–34 (1932).
[29] H. Koch and O. Horn, *ibid.*, **13,** 164–7 (1932).

Ruhrchemie [30–34] erected a pilot plant of about 1,000-tons-per-yr capacity at Oberhausen-Holten. A Ni-MnO-Al_2O_3-kieselguhr catalyst was used at 190°–210°C and atmospheric pressure. The difficulties encountered [8] were (*a*) short catalyst life of 4–6 weeks, despite an elaborate and expensive sulfur-removal process; (*b*) expensive design of converters; (*c*) loss of catalyst metals and promoters during catalyst regeneration; and (*d*) expense of conversion of the oil to marketable products.

In the period 1933–1939, an intensive and rapid development of more active catalysts occurred, with final selection of Co-ThO_2-MgO-kieselguhr (100:5:8:200 parts by weight) as the best catalyst for industrial operation.[35–39] All the German Fischer-Tropsch plants in 1938–1944 [40–48]

[30] Anon., *Iron & Coal Trades Rev.*, **129**, 542 (1934); *Times* (*London*), Nov. 19, 1934; *Chem. & Met. Eng.*, **41**, 666 (1934); *Gas- u. Wasserfach*, **77**, 798 (1934); *Fuel Economist*, **9**, 303 (1934).

[31] F. Fischer, H. Koch, and K. Wiedeking, *Brennstoff-Chem.*, **15**, 229–33 (1934).

[32] F. Fischer, *ibid.*, **16**, 1–11 (1935).

[33] A. Thau, *Colliery Guardian*, **150**, 335–7 (1935).

[34] H. Koch, *Glückauf*, **71**, 85–90 (1935).

[35] *O.P.B. Rept.* 412, May 15, 1945.

[36] A. G. Ruhrchemie, German Applic. R104,999, British Patent 518,334 (1940); French Patent 843,305 (1939).

[37] H. Heckel and O. Roelen, U. S. Patent 2,219,042 (1940); R. C. Aldrich, *Natl. Petroleum News*, **37**, R922–4 (1945).

[38] C. C. Hall and S. L. Smith, *J. Soc. Chem. Ind.* (*London*), **65**, 128–36 (1946).

[39] C. M. Cawley and C. C. Hall, *Ann. Rev. Petrol. Tech.*, **5**, 361–83 (1940).

[40] E. H. Reichl, U. S. Naval Technical Mission in Europe, *Rept.* 248–45 (1945); PB 22,841.

[41] H. V. Atwell and W. C. Schroeder, Steinkohlen-Bergwerk Rheinpreussen Moers-Meerbeck, Homberg, Germany, C.I.O.S. File XXV-6, Item 30; PB 412 (1945).

[42] C. C. Hall, Office of Gutenhoffnungshütte, A.G., Sterkrade, Ruhr, C.I.O.S. File XXVII-70, Item 30; PB 975 (1945).

[43] C. C. Hall and V. Haensel, The Fischer-Tropsch Plant of Ruhrchemie, A.G., Sterkrade-Holten, Ruhr, C.I.O.S. File XXVII-69, Item 30; PB 415 (1945).

[44] W. F. Faragher, W. A. Horne, D. A. Howes, H. Schindler, C. C. Chaffee, H. L. West, and L. Rosenfeld, Supplemental Report on Ruhrchemie A.G., Sterkrade-Holten (Oberhausen-Holten), Ruhr, C.I.O.S. File XXVII-96, Item 30, PB 1,366 (1945).

[45] R. Neumann and W. C. Schroeder, Fischer-Tropsch Plant of Hoesch-Benzin, H.G., at Dortmund, Germany, F.I.A.T. 239; PB 1,279 (1945).

[46] W. A. Horne and J. P. Jones, Fischer-Tropsch Unit at Leipzig Gas Works, Leipzig, Germany, C.I.O.S. File XXVII-68, Item 30; PB 294 (1945).

[47] C. C. Hall, Chemische Werke Essener Steinkohle, A.G., Bergkamen near Kamen-Dortmund, Germany, Inspection of Fischer-Tropsch Plant, April 19 and 20, 1945, C.I.O.S. File XXVII-54, Item 30; PB 413.

[48] C. C. Hall and A. R. Powell, Plant of Klocknerwerke, A.G., Castrop-Rauxel, Germany, C.I.O.S. File XXV-7, Item 30; PB 286 (1945).

were operating according to the Ruhrchemie process, using the Co-ThO_2-MgO-kieselguhr catalyst at 180°–200°C, at either 1 or 10 atm pressure and with two or three stages with product recovery after each stage. The average yield per cu m of $2H_2 + 1CO$ gas was 150 g of hydrocarbons ranging from propane-propylene to waxes of 2,000 molecular weight. The space velocity employed was 60–100 volumes of feed gas per volume of catalyst space per hour.

The normal synthesis gas required for the Ruhrchemie process is a mixture of 2 volumes of hydrogen and 1 volume of carbon monoxide. Recent practice in the Ruhr, when cobalt catalyst was used, showed ratios from 1.8 to 2.0 for the atmospheric-pressure process and ratios as low as 1.5 for the medium-pressure process. In the Ruhrchemie plant at Sterkrade, the medium-pressure process used a H_2/CO ratio of about 1.5 for the three stages of the synthesis. This ratio was maintained by introducing the requisite amount of "converted" water gas before each stage. In all cases, the synthesis gas contained inert constituents which seldom exceeded 20 per cent by volume.

In all plants in the Ruhr, synthesis gas was manufactured from coke in standard-design "blue water-gas" generators. In a few plants, this process was supplemented by other processes, such as cracking of coke-oven gas. In order to obtain the higher ratio of hydrogen to carbon monoxide required for the standard Fischer-Tropsch operation, it was necessary to pass a portion of the water gas, mixed with an excess of steam, through converters containing a "shift" catalyst whereby carbon monoxide was converted into hydrogen and carbon dioxide. An iron oxide-chromium oxide catalyst was used in this step at 450°–500°C. In two plants in the Ruhr, a high-hydrogen gas, produced by cracking or reforming coke-oven gas, was mixed with water gas, thereby reducing the amount of water gas to be converted.

At the Krupp Fischer-Tropsch plant at Wanne-Eickel there was a large commercial installation of the Krupp-Lurgi process for manufacture of low-temperature coke. Most of this coke was gasified in blue water-gas machines, and it yielded a hydrogen:carbon monoxide ratio of 1.35, which is closer to the desired ratio for synthesis than is obtained from high-temperature coke. Several processes for the complete gasification of coal were developed in Germany, and, although they were used for production of hydrogen for coal hydrogenation or synthetic-ammonia production, the same plants with only minor modifications could have made synthesis gas. The Pintsch-Hillebrand, the Schmalfeldt-Wintershall, and the Winkler were three such processes.

The Fischer-Tropsch process requires synthesis gas in which the total sulfur does not exceed 2.0 mg per cu m. This purification was done in

two stages: (*a*) removal of hydrogen sulfide, and (*b*) removal of organic sulfur. Removal of hydrogen sulfide is almost universally carried out by the well-known iron oxide process. At the Luetzkendorf plant, the so-called Alkazid process had been installed, in which a solution of an alkaline organic compound absorbed the hydrogen sulfide, which was then continuously stripped from the solution by steam. At Luetzkendorf, the evolved hydrogen sulfide was converted into elemental sulfur. Organic sulfur was removed in all the German Fischer-Tropsch plants by passing the synthesis gas through an alkalized iron oxide catalyst (containing about 30 per cent Na_2CO_3) at 280°C. The reaction is essentially catalytic oxidation of the organic sulfur in the gas, and it is necessary that a small percentage of oxygen (0.2–0.4 volume per cent) or air be present in the synthesis gas. When gums or gum-forming materials were present in the synthesis gas, they were removed by passage of the gas through a bed of activated charcoal before passage to the organic-sulfur-removal plant. The synthesis gas freed from hydrogen sulfide and gum-forming constituents was preheated in a heater fired with residual gas from the synthesis and then passed over the alkalized iron oxide.

The reactors in atmospheric-pressure Fischer-Tropsch plants consist of rectangular steel boxes about 15 ft long, 8 ft high, by 6 ft deep. These contain vertically placed steel sheets about 2 mm thick and spaced about 7 mm apart. The spaces between the steel plates contain the catalyst. The steel sheets are perforated by horizontally placed cooling pipes about 5 cm O.D., through which water under pressure is circulated. The cooling tubes are manifolded and connected to a steam boiler which generates steam for power and heating purposes. Approximately 5 kg of steam is generated per kg of oil product. The reactors in the medium-pressure (7–10 atm) Fischer-Tropsch plants are essentially similar to tube boilers, except that the tubes are double, with the catalyst contained in a narrow annulus between two concentric tubes. A top and bottom weld through the outer tube connects the inner tube with the boiler space, so that it is filled with cooling water. The annular layer of catalyst is 24 mm I.D., 44 mm O.D., and 15 ft high. Each reactor contains about 2,000 such tubes welded into tube sheets and is about 8 ft in diameter. The weight, volume, cooling surface, and capacity of the atmospheric- and medium-pressure converters are listed in Table 11. Table 12 shows the number of reactors in different stages at several of the German plants.

Rheinpreussen at Moers operated 96 conventional Ruhrchemie atmospheric-pressure reactors, of which 60 were normally in the first stage and 30 in the second stage. The operating temperature was in the range of 195°–200°C. The synthesis-gas-charging rate averaged about 630 cu

Table 11. Ruhrchemie Reactor Characteristics

	Atmospheric Pressure	Middle Pressure
Weight, tons	45	45
Volume (total), cu ft	650	950
Volume (catalyst), cu ft	350	350
Finned surface, sq ft	38,700	None
Tube surface, sq ft	4,300	22,600
Capacity, bbl of primary product per day	18	18

Table 12. Multistage Operation at Several German Plants

		Number of Reactors			
Name	Location	Stage 1	Stage 2	Stage 3	Pressure, atm
Hoesch-Benzin	Dortmund	40	16–20	4–8	10–15
Ruhrbenzin	Sterkrade	36	18–20	14	11
			48 total		1
Rheinpreussen	Moers	60	30	0	1
Klocknerwerke	Castrop-Rauxel		63 total		1

m per hr per reactor. The total liquid product, including gasol (C_3 and C_4), averaged 150–155 g per cu m of $2H_2 + 1CO$. The product distribution is shown in Table 13.

Table 13. Rheinpreussen Product Distribution

Constituent	Per Cent
Gasol ($C_3 + C_4$)	10.0
Gasoline	52.2
Diesel oil	26.5
Soft paraffin wax	7.6
Hard paraffin wax	3.7

Ruhrbenzin at Sterkrade-Holten operated about 48 atmospheric-pressure reactors and 72 middle-pressure reactors, all of conventional design. The normal-pressure reactors were operated in two stages on feed gas containing the usual 2 volumes of hydrogen and 1 volume of carbon monoxide. The arrangement of the middle-pressure reactors is shown in Figure 4. In this operation, the hydrogen:carbon monoxide ratio of the inlet gas to the three stages is adjusted to about 1.5 by introducing the requisite amount of converted water gas before each stage.

For stage 1 of the medium-pressure operation, the inlet-gas rate is

1,000 cu m per hr per reactor, the temperature 180°–200°C, and the gas contraction 50 per cent. Similar conditions obtain for stage 2. In stage 3, where all newly charged ovens are started, higher rates, namely, 2,000 cu m per hr per reactor, and lower temperatures, 165°–185°C, can be employed. The overall contraction is about 75 per cent, and the yield 150 g of C_3 and higher hydrocarbons per cu m of $1.5H_2 + 1CO$. The advantage of using a gas relatively deficient in hydrogen and main-

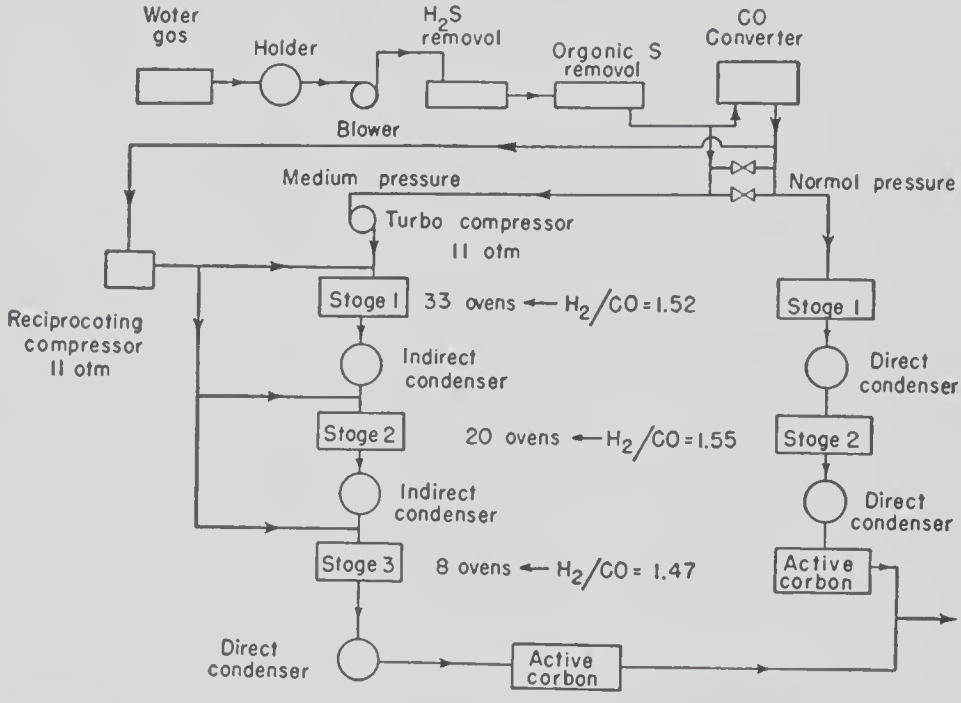


FIGURE 4–4. Flow scheme for synthesis cycle used at Sterkrade (Ruhrchemie, A.G.-Ruhrbenzin A.G., Sterkrade). Reproduced from reference 77.

taining the same proportion of hydrogen in all stages lies in combining the beneficial effects of low hydrogen partial pressure on olefin content and methane production with the efficient utilization of the carbon monoxide achieved with normal synthesis gas ($2H_2 + 1CO$). Products obtained with this method of operation are shown in Table 14. When

TABLE 14. PRODUCT AT RUHRBENZIN, STERKRADE-HOLTEN

	Weight Per Cent of Total Product	Per Cent of Olefins in Fraction
Gasol ($C_3 + C_4$)	10	40
C_5 to 170°C [a]	25	24
170°–280°C	30	9
280°–340°C (soft wax)	20	..
Residue (hard wax)	15	..

[a] Motor octane number about 45.

normal synthesis gas ($2H_2 + 1CO$) is used throughout, 14 per cent of the total hydrocarbons produced is methane, but with the above scheme, the proportion is reduced to 10 per cent. The middle-pressure synthesis yields two to three times as much wax as that at atmospheric pressure.

DESCRIPTION OF RUHRCHEMIE-TYPE PLANTS AND OPERATING DATA

Ruhrchemie A.G. Plant at Sterkrade-Holten

Water-gas, steam, and cooling-water supplies. The water gas required is produced in eleven fully automatic Humphreys and Glasgow-type generators ranging in capacity from 6,200 to 6,800 cu m per hr; allowing for the reserve capacity required for repair work and operating difficulties, the capacity of the plant is 65,000 cu m per hr. Coke ovens in the neighborhood supply the daily requirement of 100 tons of coke of 40–100-mm size and minimum carbon content of 85 per cent. To produce 1 cu m of water gas 1 kg of steam is required, of which $\frac{1}{3}$ is produced in the water jackets of the generators and $\frac{2}{3}$ in waste heat boilers. The air needed for the blow periods in the generators is supplied by nine blowers driven by steam at 18 atm pressure obtained from the waste heat boilers. The steam pressure is thus reduced to 2.5 atm before passage to the generators.

Feed water for power plant, gas generators, and the synthesis plant is demineralized in the permutit base exchange system and degassed by heating to 70°C at subatmospheric pressure to remove dissolved oxygen and carbon dioxide. Return cooling water from the synthesis plant is cooled in two atmospheric-pressure cooling towers whose combined capacity is about 6,000 cu m per hr.

Sulfur-removal plant; construction and operation. From the gasholder the water gas goes to the sulfur-removal plant. In the first part, which is known as the rough or dry purification, hydrogen sulfide is removed. The original sulfur content, 3–4 g per cu m, is reduced to 0.05–0.1 g per cu m after the dry purification. The plant consists of eight purification towers of 11.3-m diameter and 9.8-m height. Each tower contains approximately 600 tons of purifying material distributed in sixteen layers, each 400 mm high, on wooden grids. The gas passes parallel through all the layers at a velocity of about 1 m per sec; groups of three purifiers are operated in series. Cutting in and out the individual purifiers is done through water seals. The temperature is between 20° and 40°C. The purification material is Luxmasse containing 49.5 per cent moisture and having an ignition (at 475°C) loss of 5.4 per

cent. The air-dried and ignited material contains 3.4 per cent moisture, 0.8 per cent SiO_2, 56.0 per cent Fe_2O_3, 27.4 per cent Al_2O_3, 6.2 per cent CaO, 1.9 per cent SO_3, 2.2 per cent CO_2, 2.1 per cent unaccounted for. The purification material can be used about 6 months, in which time it takes up sulfur equal to 45 per cent of its own wet weight. The capacity of four purifiers is 40,000 cu m per hr, with one purifier in a group of four being refilled or standing in reserve. The spent material is sold; it is further processed and the sulfur recovered.

The rough purification is followed by a finer one to remove the combined organic sulfur. This consists mainly of COS and CS_2 at a concentration of about 0.2 g per cu m. The active life of the catalyst for the synthesis depends among other factors on the efficiency of the sulfur removal from the water gas. The sulfur compounds are removed by splitting and at the same time combining with alkaline Luxmasse at temperatures from 200° to 300°C. The fine purification plant consists of five units followed by a final purification unit. Each unit consists of a gas heater and two towers of 4.2-m diameter and 10.5-m height. Two types of tower are used. In the "basket type" the purification material is contained in six to eight separate containers which are charged externally and then lowered into the tower. The internal arrangements of the tower are such that the gas passes through the containers in parallel. The second type of tower contains two coaxial vertical sieves, between which the purification material is held in a layer 0.9–1.0 m thick. The basket type of tower can be charged more quickly, and the purification material in it has a longer life than in the other type. However, difficulty is sometimes experienced in sealing each container into place inside the tower, the gas-tight seals being made with finely divided purification material. The towers with baskets contain 60 tons and those with the screens 70 tons of purifying material. The two towers of each unit are operated in series with a heat exchanger between them to regulate the gas temperature in the second tower and to preheat the gas to the first tower. The gas heater consists of the combustion chamber, where exit gas from the synthesis is burned at a temperature of 600°–900°C, and a bundle of steel tubes made of heat-resisting steel at the lower (hot) end and of ordinary steel at the upper (cooler) end. The incoming gas enters the heat exchanger, then passes through the tubes of the preheater, and from there goes to the first tower. Upon leaving this tower the gas is cooled in the heat exchanger and passes to the second tower. The normal capacity of each unit is 17,000 cu m per hr, the maximum capacity 20,000 cu m per hr. The hourly space velocity is about 200. From these five groups of purifiers, the gas passes through two final purification towers arranged in parallel. No preheating is

necessary. These two purifiers are used as a safety measure, because, after a tower in the main purification system is refilled, an induction period exists during which the new material is not functioning efficiently.

Some operating data for sulfur removal are given in Table 15. The life of a unit under normal load is about 40 days, after which the material in the first tower is completely spent. The second tower is then used as the first.

TABLE 15. RUHRCHEMIE ORGANIC-SULFUR-REMOVAL OPERATING DATA

Temperature, °C			Sulfur, g per 100 cu m					
			Before Tower 1		Before Tower 2		After Tower 2	
Days	Tower 1	Tower 2	Organic Sulfur	H_2S	Organic Sulfur	H_2S	Organic Sulfur	H_2S
2	200	180	2.3	20.2	<0.05	4.2	<0.05	<0.05
18	230	200	3.1	20.1	<0.05	5.2	<0.05	<0.05
33	255	215	3.4	20.4	<0.05	5.2	<0.05	<0.05
43	270	220	3.5	20.1	0.09	6.2	0.12	0.2

The fine purification material consists of a mixture of iron hydroxide and soda. When air-dried, this mixture contains 8.0 per cent moisture, 59.5 per cent Fe_2O_3, 29.0 per cent Na_2CO_3, and 3.5 per cent SO_3. The granule size is 10–15 mm. The spent material contains 33 per cent Na_2SO_4, 0.3 per cent Na_2SO_3, and 4 per cent Na_2CO_3.

Before the water gas enters the hydrogen sulfide-removal system, air is added to the gas to give it an oxygen content of 0.4 per cent. Of this, 0.2 per cent is consumed in the hydrogen sulfide-removal system, the remainder in the organic sulfur removal by the formation of sodium sulfate.

Hydrogen production (CO conversion); construction and operation. For the hydrocarbon synthesis a gas is required in which the ratio of carbon monoxide to hydrogen is 1:2, whereas in water gas this ratio is only 1:1.3. For this reason the catalytic water-gas process is used to produce the additional required hydrogen. About one-third of the water gas is treated. The carbon monoxide in the water gas reacts with steam to give carbon dioxide and hydrogen as given in the following equation:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

The catalyst is Fe_2O_3, containing 6.6 per cent Cr_2O_3, 22.2 per cent CaO, 6.4 per cent MgO, 6.2 per cent SiO_2, 3.0 per cent Al_2O_3, 6.1 per cent CO_2, 2.3 per cent SO_3, and consists of hard granules 0.5–0.75 in. in size. The converter, 3.2 m diameter, contains 26–28 tons of catalyst in four layers, each 750 mm high. Below the converter is a heat exchanger with an area of 1,400 sq m. Converter and heat exchanger have a combined height of 14.50 m. The water gas, before reaching the converter, passes through a saturation tower (2.40 m diameter, 27 m height) where it is saturated at 70°C. The water used in the saturation tower comes from the cooler and cools the converted water gas leaving the converter. A steam injector, operating at 9 atm gauge, forces the gas from the saturation tower through the heat exchanger into the converter, supplying at the same time the required steam for the reaction. The heat exchanger transfers heat from the converted gas to the incoming gas. The converted gas finally passes through a cooling tower (3.10 m in diameter, 27 m in height, Raschig rings packing in five layers) and leaves the plant at 25°–30°C. In the cooler and saturator some hydrogen sulfide is formed through the action of certain bacteria on the calcium sulfate in the water. Since the converted gas passes immediately into the hydrocarbon synthesis reactors, the hydrogen sulfide formation has to be eliminated. This is done by circulating the cooling water in a separate circuit over an atmospheric-pressure cooling tower. The condensation of the excess steam from the converter provides a sulfate-free condensate for the cooler and saturator. During any irregularities in the water circulation the action of the bacteria is inhibited by the addition of zinc chloride.

The reduction of steam by carbon monoxide is exothermic and takes place at temperatures from 420° to 480°C. The catalyst in the first layer is at 370°C. After the second layer a residue-free condensate is injected to control the rising temperature and save steam. An increase in excess steam is required with a rise in temperature to cause the reaction to go to the right. In commercial practice 0.8–1.0 kg of steam per cu m of water gas is required when saturation and condensate injection is not employed. By saturation and injection the consumption is reduced to 0.6–0.7 kg per cu m. If condensate with a residue on evaporation of less than 2–5 mg per l is not available, the injection has to be omitted, as a higher residue content in the condensate causes blocking of the catalyst. Crust formation on the catalyst due to the salts in the steam and condensate, and the deterioration of the catalyst from mechanical action of the gas, limit its life to about 2 years. If after this period the catalyst is screened to remove fines, its life is extended to 3–4 years. The first heating of the catalyst to reaction temperature of

370°–400°C is done with flue gas from a small gas burner. On passing water gas and steam over the catalyst, it is first reduced and after a few hours is ready for normal operation. Before an extended shutdown, the catalyst is oxidized with a mixture of steam and air, or preferably nitrogen and air. The plant consists of five converters each of 6,000-cu-m-per-hr capacity, two saturators, three coolers (one reserve), and the necessary pumps for the cooling-water circulation and wetting of the saturators.

Blower house. Three gas blowers of total capacity 160,000 cu m per hr draw all the water gas through the hydrogen sulfide-removal units and force it into the synthesis plant. Under normal load two 40,000-cu-m-per-hr gas blowers or one 80,000-cu-m-per-hr blower are in operation; hence, the reserve capacity is 100 per cent. The hydrogen sulfide scrubbers are placed on the suction side of the gas blowers to enable removal, in these scrubbers, of the remaining dust (20 mg per cu m) in the water gas, because this dust deposits on the blower impeller, causing serious damage. The disadvantage of this method is the presence of a negative pressure in the hydrogen sulfide scrubbers (minimum allowable, -500 mm H_2O). This condition also reduces the capacity of the gas blowers, since they are designed for a suction pressure of 100 mm water instead of -500 mm water now present. In view of this condition it was planned to install an electric dust precipitator so that the gas blowers could be installed before the hydrogen sulfide scrubbers. Two air blowers of 1,000-cu-m-per-hr capacity serve to supply the air in the sulfur-removal reactions.

Compressor house. Four turbocompressors each of 20,000-cu-m-per-hr capacity and one of 35,000-cu-m-per-hr capacity supply synthesis gas for the medium-pressure synthesis. For the normal load of the medium-pressure synthesis, about 50,000 cu m per hr of synthesis gas has to be compressed. This requires either the operation of three 20,000-cu-m compressors or the 35,000-cu-m and a 20,000-cu-m compressor. One 20,000-cu-m compressor is used on the converted water gas which goes through the carbon dioxide scrubbers. Including the 35,000-cu-m compressor installed for the olefin synthesis, the reserve capacity is 100 per cent. In front of the compressor house are two spray cooling towers, 4 m in diameter and 16 m high, which cool to 25°C the hot gas coming from the organic-sulfur-removal units. Heat exchangers transfer part of the heat to hydrogen going to the atmospheric-pressure synthesis. These coolers are in the same water circuit as the carbon monoxide conversion plant, because also in them, hydrogen sulfide formation through bacterial action must be averted. Finally, there are two pump-turbine units to pump the converted water gas through the carbon dioxide

scrubbers to the medium-pressure synthesis. The pumps supply two scrubbing towers of 3-m diameter, 16-m height, and filled with 50-mm Raschig rings. Water under pressure flows from the scrubbers over the turbine to the degassing tower which has a cross-sectional area of 18 by 18 m and is 30 m high. Four ventilators of 450,000-cu-m-per-hr capacity ventilate the tower. This tower was used temporarily also for the cooling water of the carbon monoxide conversion plant, and a separate indirect cooling system was planned for the carbon monoxide plant. The temporary procedure resulted in a higher water temperature and in a less effective scrubbing out of carbon dioxide from the converted water gas. The scrubbing towers have a capacity of 10,000 cu m per hr of gas and 1,400 cu m per hr of scrubbing water. The carbon dioxide concentration is decreased from 29 to 10 per cent; at the same time there is a loss of 2.5 per cent of carbon monoxide and hydrogen based on the volume of gas entering the towers. Following the scrubbing towers are a spray separator and a floating valve which prevent water discharge into the gas lines.

The carbon dioxide (about 3,500 cu m per hr) scrubbed out from the converted water gas has so far not been used. It was planned to recover a carbon dioxide-rich gas by reducing the pressure in a larger receiver (already present) through which the water from the scrubbing towers would pass before entering the degassing towers. Carbon dioxide is used as a safety gas in many parts of the plant.

Hydrocarbon synthesis. Into the hydrocarbon synthesis reactors, purified water gas with the required ratio of hydrogen:carbon monoxide is fed by blowers and compressors for the normal- and medium-pressure synthesis, respectively. The synthesis reaction is:

$$n\mathrm{CO} + 2n\mathrm{H_2} \rightleftharpoons (\mathrm{CH_2})_n + n\mathrm{H_2O}$$

Because of the large amount of heat evolved, the main problem in design of the reactors concerns rapid and efficient heat transfer. Synthesis temperature is controlled by regulation of the steam pressure in the water-filled pipe system of the reactors. The reaction temperatures are 180°–200°C and are kept within 0.5°C limits. The catalyst consists of cobalt-magnesium oxide-thorium oxide and is supported on kieselguhr. The grain size of the catalyst is 2–3 mm. The composition by weight is as follows: 30 per cent Co, 2.5 per cent MgO, 1.5 per cent ThO_2, 66 per cent kieselguhr. The volume of catalyst per reactor is about 10 cu m, containing about 900 kg cobalt. The catalyst is obtained from the Ruhrchemie-Katalysatorfabrik in the reduced state, and it is therefore highly sensitive to oxidation. For this reason it is delivered to the plant in closed buckets under an atmosphere of carbon dioxide. Overhead

cranes on tracks empty the buckets into the top of the reactors. The cranes have a carrying capacity of 60 tons and can lift an entire reactor which weighs 46–49 tons.

The first technical large-scale Fischer-Tropsch synthesis was carried out at atmospheric pressure in Sterkrade-Holten by the Ruhrchemie. The synthesis building houses, in the east half, 52 low-pressure reactors. Each reactor is 5 m long, 1.50 m wide, and 2.50 m high and is a sheet-metal box through which 630 34-mm-O.D., 29-mm-I.D. parallel pipes pass. At right angles to the pipes are 555 sheet-metal plates through which the pipes pass. These plates are 1.6 mm thick, and the distance between them is 7.4 mm. The open space between the plates contains the catalyst, and removable screens at the bottom prevent the grains from falling into the oil sump below the reactor. The water tubes are connected to tube sheets at each end of the chamber. The tube sheets are united in a steam drum. An electric controller regulates the steam pressure in the steam drum which in turn controls the temperature in the water tubes. There is a steam drum for every 2 reactors. Heat from the reaction transferred to the water in the tubes is equivalent to 5 kg of steam per kg of liquid product. The allowable pressure in the catalyst space is 0.3 atm gauge and in the water tubes 30 atm gauge.

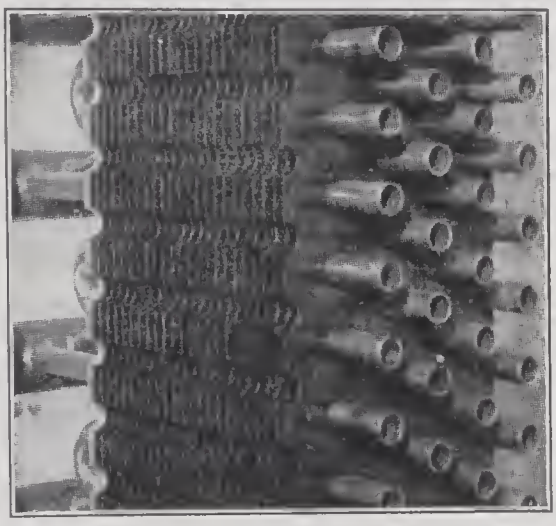


FIGURE 4–5. Atmospheric-pressure Fischer-Tropsch converter.

The reactors are constructed of ordinary steel. The tubes are expanded into the plates either by hydraulic pressure or by drawing through the tubes a steel ball of slightly larger diameter than that of the tubes. Ruhrchemie has reactors made by both methods and has found that those made in the second way are more satisfactory. In the preferred type of construction of the cooling system, each cooling tube is fitted directly into the water chambers at each end of the reactor. This construction is illustrated in Figure 5. In some of the Ruhrchemie ovens adjacent tubes are combined to give tube coils of different sizes, and only each end of each coil is connected to the end water chambers. In ovens of this type of construction, overheating occurred more frequently than in the type illustrated in Figure 5.

The hydrocarbons of the synthesis consist of gaseous, liquid, and solid products. Gasol ($C_3 + C_4$ mostly), light naphtha, and oil leave the

reactors as vapor in the exit gas and are recovered in the equipment that follows. Some paraffin wax remains with the catalyst and accumulates to 50 per cent of the catalyst weight. The essential features of the atmospheric-pressure synthesis are outlined in Table 16 for the Ruhrchemie A.G. plant at Sterkrade-Holten [49, 50] and for the Rheinpreussen plant at Moers-Meerback.[41] The analysis of the residual gas from the Rheinpreussen plant appears to be incorrectly reported; the hydrogen and carbon monoxide contents are too low to fit the data on yield of products.

TABLE 16. OPERATING DATA, ATMOSPHERIC PRESSURE SYNTHESIS ON COBALT-THORIA-MAGNESIA-KIESELGUHR CATALYSTS

Company	Ruhrchemie, A.G.			Steinkohlen-Bergwerk		
Location of plant	Sterkrade-Holten			Rheinpreussen, Moers-Meerback		
Date of operation	1943–1944			1941–1942		
Stage number	1	2	1 + 2	1	2	1 + 2
Synthesis gas, 1,000 cu m per hr	..	..	15.5–17.5	..	..	66.1
Number of reactors in use	18–21	9–11	27–32	60	30	90
Gas analyses, volume per cent	In gas	In gas	Residual gas from 2d stage	In gas	In gas	Residual gas from 2d stage
CO_2	14.4	29.6	44.2	8.9	21.0	34.4
C_nH_m	0.0	1.5	2.0	0.0	0.3	1.1
CO	26.7	17.8	9.7	26.2	15.7	3.3(?)
H_2	53.2	33.7	16.0	51.5	28.7	7.0(?)
CH_4	0.4	7.0	13.2	0.7	7.6	14.9
N_2	5.3	10.4	14.9	12.4	26.6	39.2
Contraction, per cent	49.3	31.5	65.4	52.8	32.1	68.3
	Stages 1 + 2			Stages 1 + 2		
	Boiling Range, °C	g per cu m of $CO + 2H_2$	Per Cent of CO Reacted	Boiling Range, °C	g per cu m of $CO + 2H_2$	Per Cent of CO Reacted
Product distribution						
CO_2	....	.....	4.9	....	....	7.5
$C_1 + C_2$	....	28.1	15.4	....	....	15.5
Gasol	....	21.9	10.2	....	21.2	9.9
Gasoline	To 200	76.2	35.5	To 160	63.6	29.4
Diesel oil	200–320	33.2	15.5	160–320	44.2	20.6
Soft wax	320–360	9.9	4.6	320–360	10.7	5.0
Hard wax	Above 360	3.7	1.8	Above 360	3.5	1.6
Total liquids and solids	....	123.0	67.6	....	122.0	66.5
CO unconverted, per cent of total CO	12.1			10.5		

[49] T.O.M. Reel 35, Bag 3,440, Item 83.

[50] C. C. Hall and S. R. Craxford, Additional Information Concerning the Fischer-Tropsch Process and Its Products, *B.I.O.S. Final Rept.* 1722, Item 22; PB 93,498.

The procedure used by Ruhrchemie in starting a freshly charged reactor and maintaining its activity is outlined as follows:

1. The reactor is always started in stage II, by heating up to 100°–125°C after flushing with stage II feed gas. It is kept at that temperature for 5 hr without gas flow.

2. Gas flow is then started at the rate of 250 cu m per hr, while the temperature is increased at the rate of 5°C per hr until 160°C is reached, and then at 1°C per hr until a contraction of 60 per cent is reached.

3. The gas rate is then increased to 500 cu m per hr, which causes a drop in contraction to 40 per cent. The temperature then is increased 1°C per hr until a 45 per cent contraction is obtained. The gas rate then is increased to 1,000 cu m per hr, which again results in a drop in contraction to 40 per cent. A 45 per cent contraction is reached by again increasing the temperature 1°C per hr.

4. The flow of gas is increased to its final value of 1,400 cu m per hr, and the temperature increased 1°C per hr until 55–60 per cent contraction occurs. Thereafter, this degree of contraction is maintained by increasing the temperature when necessary to compensate for any decrease in catalyst activity.

5. When a reaction temperature of 190°–191°C is reached, the catalyst is regenerated by extraction with solvent, which may be followed by treatment with hydrogen. The converter is again put into operation in stage II at 175°C for 2 days. It is then transferred to stage I.

6. After 30 days in stage I, 192°C is reached. Regeneration of the catalyst lowers this to 180°C. Succeeding regenerations are made when the synthesis temperature reaches 193°, 195°, 198°, and 200°C after 50, 70, 90, and 110 days, respectively.

The normal rate of temperature increase for both stages is 1°C every 2–3 days. In stage I the initial gas rate of 1,000–1,200 cu m per hr is decreased about 100 cu m per hr per month until 800 cu m per hr is reached. Thereafter the gas rate is maintained at that value. For various reasons the ideal schedule outlined above could not be followed at Sterkrade-Holten. The chief reason was insufficient supply of water gas. The medium-pressure plant and full-scale experimental plants were favored with an adequate gas supply, and any deficiency resulted in an inadequate supply to the atmospheric-pressure plant.

In the periodic catalyst regenerations a fraction of the oil product boiling in the range 140°–200°C is sprayed into the top of the reactor which is kept at 100°C. The extraction is continued (for 12–15 hr) until the wax content of the catalyst has been decreased to 1–2 per cent. Usually 2–2.5 tons of wax is recovered from one reactor. This solvent treatment ordinarily is adequate to regenerate the catalyst as indicated

by the appreciably lower operating temperature necessary to maintain a 55–60 per cent contraction. If the catalyst does not respond satisfactorily to this treatment, it is exposed to a flow of 1,000 cu m per hr per reactor of hydrogen at about 200°C for 7–10 hr at atmospheric pressure. The average industrially useful life of a charge of catalyst is about 4 months. This can be prolonged to 6 or 8 months, if desired, by more frequent regenerations. At the end of 6–8 months the catalyst does not respond to further solvent extractions and treatment with hydrogen at 200°C. Ruhrchemie reports [50] that further revivification can be achieved by a procedure which is essentially a rereduction of the catalyst. This procedure consists in passing dry hydrogen or 75 per cent H_2 + 25 per cent N_2, free from CO and CO_2, over the catalyst at 2,000 space velocity per hour. The temperature is kept at 200°C for 1.5 hr and then rapidly increased to 450°C during the next 2 hr and maintained at 450°C for an additional 2 hr. This treatment removes about 98 per cent of the wax and carbon, about 80 per cent of the sulfur, and about 50 per cent of the oxygen content of the spent catalyst. By means of a combination of such rereduction and solvent extraction the catalyst life may be extended to 12–14 months. This has not been done on a commercial scale by Ruhrchemie because of shortage of hydrogen. In rereduction the hydrogen cannot be recycled as in the reduction of a fresh catalyst because of the methane content of the off gas. Another reason is the necessity of removing the charge from the converter because the temperature of the rereduction, 450°C, cannot be reached in the commercial reactors. The rereduction procedure was thoroughly tested, however, in the laboratory not only by Ruhrchemie but also by Hall and Smith [38] at the British Fuel Research Laboratory. In the commercial plants, the spent catalyst is dropped into a trough under the reactor and transported by a chain conveyor to drums for shipment to the catalyst factory. Here it is processed for recovery of its cobalt and thoria content.

The medium-pressure synthesis was preferred in Germany because of the appreciably higher yield of oil per cubic meter of synthesis gas and longer life (6–9 months) of catalyst without any reactivation. Because of the solvent action of liquid products condensed at 7–10 atm on the catalyst, the wax was continuously carried out of the reactor. Another advantage of medium-pressure operation was the much higher proportion of wax in the product. This product was preferred in Germany in 1938–1944 as cracking stock to supply olefins for synthetic lubricating oils and chemicals. The medium-pressure reactors are of different construction from those for the low-pressure synthesis. In a vertical drum of 2.7-m diameter are fitted about 2,000 double tubes of 4.5-m length.

The double tubes consist of 24-mm-O.D., 21-mm-I.D. pipes fitted concentrically into 48-mm-O.D., 44-mm-I.D. pipes. A cross section of one double tube is shown in Figure 6. The catalyst lies in the annular space while water flows both on the outside of the larger tubes and the inside of the smaller ones. Wire-screen sections are hinged at the bottom of

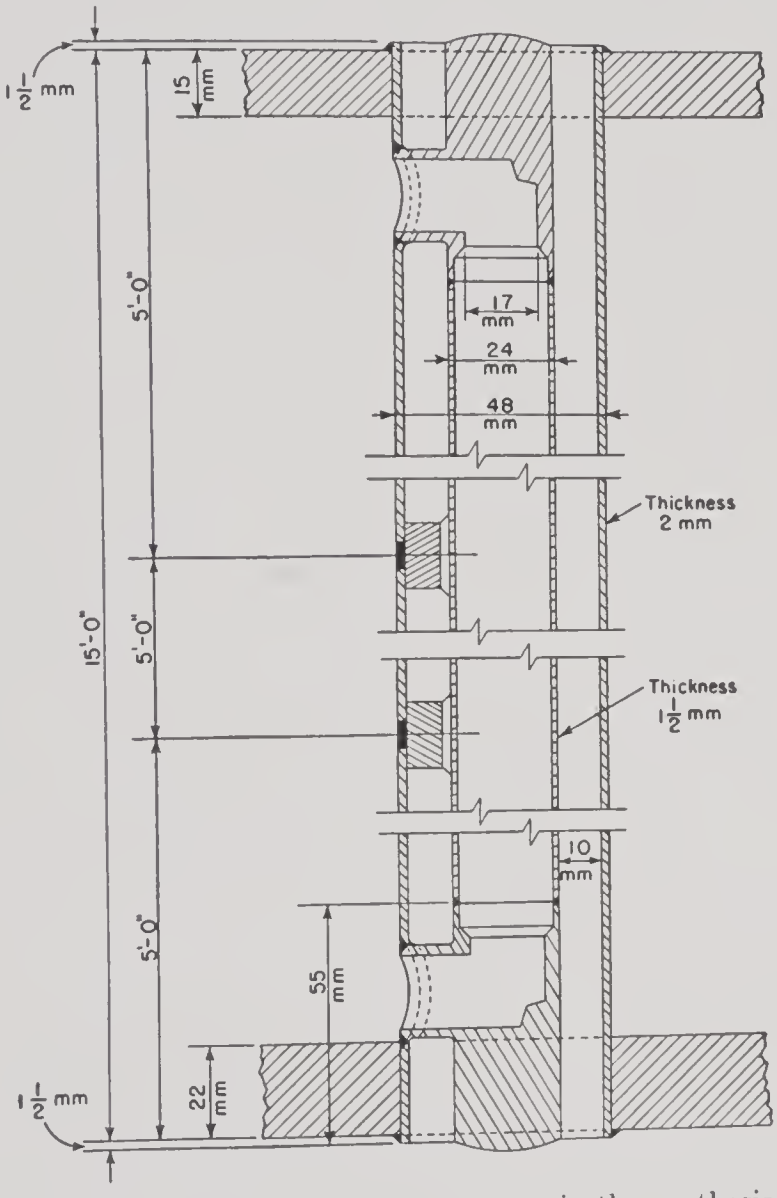


FIGURE 4–6. Detail of double tube for converter in the synthesis at 10 atm.

the drum to retain the catalyst. The converters are arranged in units of four, each unit having a steam drum. The allowable pressure in the gas system is 15 atm gauge, that in the water system 25 atm gauge. In the west part of the synthesis building there were seventy-three reactors; two of these were experimental, one a "Wulstofen" which had a self-contained annular-shaped steam drum fitted around the top, and the other a "Drucklamellenofen" of the same design as the low-pressure reactors but of heavier construction to withstand the pressure of the medium-pressure synthesis.

The major difficulties encountered in use of the commercial double-tube reactors were corrosion at welded surfaces between the tubes and the tube sheets or "headers," and poor heat transfer in the top 10 cm of the tubes. Corrosion can be reduced by use of condensed steam rather than "softened" water. Poor heat transfer at the top 10 cm of the double tubes resulted in overheating and rapid deposition of carbon in this section. Ruhrchemie found it desirable to leave the top 10 cm empty of catalyst. Although the "Wulstofen" reactor provides adequate heat transfer in the top 10 cm of the tubes, its construction is more difficult and more expensive than that of the normal, double-tube reactor.

Ruhrchemie started freshly charged medium-pressure reactors in stage 3. They are put under pressure of 9–10 atm of stage 3 feed gas (see Table 17) and heated to 125°C. Gas flow is then started at 500 cu m per

TABLE 17. MEDIUM-PRESSURE (9–10 ATM) SYNTHESIS ON COBALT-THORIA-MAGNESIA-KIESELGUHR CATALYST IN THREE STAGES IN RUHRCHEMIE COMMERCIAL PLANT, OPERATING DATA FOR THE PERIOD NOVEMBER 1943 TO FEBRUARY 1944

Stage number	1		2		3		
Temperature, °C	198.9		196.4		196.4		
Number of reactors	33.4 [a]		19.8 [a]		8.2 [a]		
Feed, cu m per reactor per hr	1,114		1,120		1,915		
Gas analyses, volume per cent	Feed	End	Feed [b]	End	Feed [b]	End	Shifted
CO_2	6.9	14.7	14.7	28.0	25.0	36.3	16.8
C_nH_m	0.0	0.9	0.0	1.15	0.0	1.25	0.0
CO	34.7	35.0	27.5	23.9	20.2	14.0	5.6
H_2	52.7	33.9	42.5	18.2	29.8	11.5	71.9
CH_4	0.4	5.0	4.2	11.3	9.2	15.7	0.4
N_2	5.2	10.5	9.4	17.4	14.8	21.0	5.3
Contraction, per cent	50.4		45.8		29.7		
Conversion	CO	H_2	CO	H_2	CO	H_2	
Per cent	50.5	68.2	52.9	77.2	51.3	73.0	
CH_4, per cent of CO converted	11.9		13.2		17.9		
CH_4, g per cu m of total $CO + H_2$ fed to the plant	13.6		7.1		3.2		

Liquid products, gram per cubic meter of total $CO + H_2$ fed to plant, stages 1 + 2 + 3: 137.4.

Gasol, gram per cubic meter of total $CO + H_2$ fed to plant, stages 1 + 2 + 3: 17.3.

[a] Fractions of reactor number caused by time-number averages.

[b] The analyses of feed gas to the second and third stages are not consistent with the volumes (calculated from contractions, feed-gas rate of previous stage, and ratio of number of reactors in the two stages) and analyses of end gases and of shifted gas used to prepare these feed gases.

hr and the temperature increased at the rate of 5°C per hr until 160°C is reached; then it is increased 1°C per hr until the gas contraction is 45 per cent. The gas rate is then increased to 1,000 cu m per hr and the temperature again increased at the rate of 1°C per hr until the gas contraction is again 45 per cent. The gas rate is again increased to the normal value of 1,800–2,000 cu m per hr and the temperature raised 1°C per hr until the gas contraction is 29–30 per cent. Temperatures in the three stages are set so as to maintain contractions of about 50 per cent in stage 1, 45 per cent in stage 2, and 30 per cent in stage 3. When the temperature in a stage 3 reactor reaches 203°C, it is shifted to stage 2, where the synthesis proceeds at 185°–188°C. It is kept in operation in stage 2 until the temperature reaches 197°C, when it is transferred to stage 1, and here the synthesis proceeds at about 180°C. In stage 1, the maximum operating temperature is set at 203°C, and when this is reached the catalyst is discharged. During the useful life of the catalyst the gas rate is slowly reduced until it is about 800 cu m per hr after 6–7 months. It is aimed to set operating conditions so that about the same space-time-yield is obtained in each stage. The data given in Table 17 comprise a summary of the operating conditions and yield for the period November 1943 to February 1944, inclusive, at the Ruhrchemie.[20] A similar set of data for operation at the Hoesch plant in March 1944 is given in Table 18.[50] Although there are some inconsistencies in both tables, they do not seriously affect the comparisons made below.

The data in Table 17 suggest the following comments on the influence of "inerts," *ie*, CO_2, N_2, and CH_4. Comparison is made of data for stages 2 and 3, which were operated at the same average temperature (196.4°C). In stage 2 with the initial concentration of $CO + H_2$ at 0.7 of the feed gas the fraction of the $CO + H_2$ converted was 0.699. In stage 3 with the initial concentration of $CO + H_2$ at 0.5 of the feed gas the fraction of $CO + H_2$ converted was 0.694. As the space velocity in stage 3 was 170 per cent of that in stage 2, the fraction of $CO + H_2$ converted would be expected to be much lower in stage 3 than in stage 2 if there were no specific effect of inerts. It appears that the presence of inerts increases the yield per unit volume of $CO + H_2$ in the feed gas. This is in accord with the conclusions drawn from the data of Table 5 on the effect of dilution of synthesis gas with nitrogen.

The data in the last two rows of Table 17 indicate an increased percentage conversion of CO to methane with increasing methane content of the feed gas, although the actual number of grams of methane produced per cubic meter of total $CO + H_2$ fed to the plant is lower in stage 2 than in stage 1 and lower in stage 3 than in stage 2. Comparison of Tables 17 and 18 shows a somewhat lower methane production at the

TABLE 18. MEDIUM-PRESSURE (9–10 ATM) SYNTHESIS ON COBALT-THORIA-MAGNESIA-KIESELGUHR CATALYST IN THREE STAGES IN HOESCH COMMERCIAL PLANT AT DORTMUND, GERMANY, OPERATING DATA FOR MARCH 1944 [a]

Stage number	1		2		3			
Temperature, °C	198.1		195.4		198.7			
Number of Reactors	40.0		16.0		8.0			
Feed, cu m per hr per reactor	928		1,238		2,037			
Gas analyses, volume per cent	Feed	End	Feed [b]	End	Feed [b]	End	Water Gas	Shifted
CO_2	7.81	17.50	15.38	26.94	22.56	33.45	7.86	6.71
C_nH_m	0.0	0.80	0.80	1.18	1.10	1.40	0.0	0.0
CO	33.66	30.99	27.94	23.21	21.00	14.60	37.74	13.36
H_2	52.47	31.35	39.41	17.80	29.60	11.30	48.39	73.18
CH_4	0.40	6.79	5.75	12.51	10.26	16.94	0.30	0.4
N_2	5.66	12.39	10.72	18.36	15.48	22.31	4.97	6.35
Contraction, per cent	56.2 [c]		44.2 [c]		36.0 [c]			
Conversion	CO	H_2	CO	H_2	CO	H_2		
Per cent	59.6	73.8	53.7	74.8	55.5	75.6		
Conversion, CO + H_2 per cent	69.2		68.2		74.2			
CH_4, per cent of CO converted	12.8		8.3		5.1			
CH_4, g per cu m of total CO + H_2 fed to the plant	17.0		4.2		1.4			

Liquid products, grams per cubic meter of total CO + H_2 fed to plant, stages 1 + 2 + 3: 143.5.
Gasol, grams per cubic meter of total CO + H_2 fed to plant, stages 1 + 2 + 3: 18.1.

[a] Temperatures, number of reactors, feed per reactor, and contraction data from Table 18 of reference 50. Gas analyses taken from Table 20 of reference 50.

[b] The analyses of feed gas to the second and third stages are not consistent with the volumes (calculated from contractions, feed-gas rate of previous stage, and ratio of number of reactors in the two stages) and analyses of end gases and of shifted gas used to prepare these feed gases.

[c] Contraction calculated from special N_2 determinations not given in Table 21.

Hoesch plant [50] (Table 18) and a correspondingly higher oil yield. As there is no obvious explanation based on data in Tables 17 and 18 for this difference, it must be due to better operating techniques at the Hoesch plant. Freshly charged reactors were started in stage 3 at this plant and kept there for 1 month. Starting temperature was 170°C, which was increased to 200°C in 4 days. The initial gas throughput of 2,000 cu m per hr was decreased to 1,500 cu m per hr by the end of the first month. Upon switching the reactor to stage 2, the temperature was lowered to 180°C and the gas rate to 1,200 cu m per hr. During the first month in stage 2 the temperature was raised to 195°C. The gas rate was lowered slowly so as to maintain a constant contraction during the 5–6 months in stage 2; the rate at the end of this period was about 900 cu m per hr. The reactor was then switched to stage 1, starting at 196°C and 900–1,000 cu m per hr and finishing in 1–2 months at 200°C and 600 cu m per hr.

In the Ruhrchemie medium-pressure plant, oil vapors and steam were condensed after each stage. To prevent separation of spray in the reactors the gas was preheated to 160°C between stages. Mild steel, which is not resistant to the attack of aqueous solutions of the organic acids formed, was used in this plant. It is necessary therefore to insulate the exit gas lines sufficiently to prevent condensation of solutions of corrosive acids in them.

Some interesting observations on starting the synthesis at 10 atm on cobalt catalysts are presented in Table 19.[51] After about 90 hr, when the contraction was about 50 per cent and the temperature 180°C, an appreciable amount of very dark-colored wax was observed in the prod-

Table 19. Black Wax from Initial Product of Medium-Pressure Synthesis

Time from Start, hr	Temperature, °C	Contraction, per cent	Product Characteristics
13	164	11	No liquid product
14	165	11	Small amount of clear oil
18	167	25.1	Clear oil
24	170	27	Oil + water
30	173	32.8	Oil + water
37	175.5	35.3	Oil + water
52	175.5	44.3	Oil + water
61	175.5	44.0	Oil + water + film of dust
73	176	43.8	Oil + water + film of dust
82	178	39	Water, oil + small amount of wax
88	178	49.5	Water, oil + small amount of wax
91	179.8	47.5	Water (25–50 mg Co per l), oil, black wax (1.15 per cent ash)
102	183	58.2	Water (25–50 mg Co per l), oil, wax (3.34 per cent ash)
117	184.4	55.9	Water (25–50 mg Co per l), oil, wax (3.3 per cent ash)
137	184.4	55.9	Water (25–50 mg Co per l), oil, wax (1.5 per cent ash)
142	184.4	60.6	Water (25–50 mg Co per l), oil, gray-black wax (0.08 per cent ash)
152	184.4	60.6	Water (25–50 mg Co per l), oil, gray-white wax
157	184.4	60.6	Water (25–50 mg Co per l), oil, pinkish white wax
175	184.4	60.6	Water (25–50 mg Co per l), oil, white wax (0.07 per cent ash)
360	184.4	60.6	Water (25–50 mg Co per l), oil, white wax (0.0 per cent ash)

[51] T.O.M. Reel 33, Bag 3,440, Items 21–c and 22.

uct. The ash content of the wax reached a maximum of about 3.3 per cent at about 100 hr of operation and decreased, thereafter, until it was about 0.07 per cent at 175 hr. The color of the wax became progressively lighter as the ash content decreased.

A sample of topped black wax containing 5.5 per cent of ash was exhaustively extracted with benzol. The black material insoluble in benzol was thus freed from the bulk of the wax. The insoluble material was 25 per cent of the original sample and contained 22 per cent ash. This ash contained 11.7 per cent carbon, 3.95 per cent cobalt, 0.22 per cent magnesia, 3.9 per cent of silica.

Condensation of oil and water vapors. The condensation in the low-pressure synthesis was done by direct cooling. The first stage had a tower of 3.45-m diameter and 25.2-m height; the second stage a tower of 2.85-m diameter and the same height. Both towers had acid-resistant linings. To resist acid attacks, water and product lines were made of aluminum, and pumps and fittings of alloy steel. Both towers had four layers of Raschig rings and are wetted in three stages. The circulating water passed through a special cooling tower. The circulating pumps of 130-cu-m-per-hr capacity were housed with the oil pumps in a pump house. The oil and water from the towers passed through a water seal and collected in separators of 4-m diameter and 2.2-m height from which the oil and water overflowed separately into receivers. The oil passed through meters to the still feed tank and the water was sent to the cooling tower. By adding a small amount of fresh water to the circulating water the acid content was held to the allowable concentration (*p*H 6.5). As there was no commercial-scale recovery of water-soluble organic compounds, a continuous purge of a fraction of the circulated water was necessary. Separators and receivers were installed in an open pit near the towers. This pit contained also a reciprocating steam-driven pump for transferring the oil to the still heaters.

In the medium-pressure plant condensation was effected by indirect cooling because the products do not separate well from water owing to the presence of high-molecular-weight acids. After each stage and before each condenser was a neutralization tower filled with Raschig rings followed by a scrubbing tower (with split ring plates). Into the scrubber a 1.5 per cent solution of soda was pumped at the rate of 2–3 cu m per hr to neutralize the acids in the products. To facilitate separation of oil and water, 3 per cent NaCl was added to the soda solution. Because the scrubbing tower had been found to be sufficient, the neutralization tower, originally intended to be used in series with the scrubber, was not operated. The scrubbing solution flowed off together with the oil and water of the reaction. The *p*H of this mixture was held at 5.0–6.0.

Each of the condensers after the first and second stage had a cooling area of 400 and 300 cu m, respectively. After each stage was a pressure vessel for spray separation. The collected liquid flowed over skimming pots (Schimmertöpfe) to a common pipe which led into a sump. The off gases were scrubbed with water and then sent to the adsorption plant (activated charcoal). The oil and reaction water flowed into a separation basin made of concrete and consisting of four chambers arranged in series. The separated oil was pumped through meters to the refinery, the water to a settling basin. The oil-free water flowed from the settling basin to the canal. Oil and emulsion from the settling basin, and oil and paraffin residues accumulating in any part of the plant were heated in a special chamber and filtered. The recovered oil was sent to the refinery.

Mild steel was used in the construction of the pressure condensation plant. The neutralization with the soda solution proved to be sufficient to avoid excessive corrosion. The tubes of the pressure condensers were attacked quite strongly on the outside by the cooling water and therefore were copper plated on the water side, but corrosion was still present at the ends of the tubes near the header. A direct cooling system, of more recent design, was used for condensation in the third stage of the medium-pressure synthesis. Soda solution was circulated through a bubble plate scrubber and through an indirect cooler. The condensate and soda solution flowed from the scrubber into a separator out of which the oil flowed to the refinery, and the soda solution was recycled to the scrubber. By addition of fresh soda solution, the *p*H of the circulating solution was maintained at 6.0–7.0. After the third stage the pressure of the exit gas was released by use of an automatic control valve, and the gas then passed to the active charcoal adsorption plant. In the medium-pressure reactors the higher-boiling hydrocarbons condensed to liquids which were separated from the vapors and gases before these entered the condensation plant. The separated liquid ran into a common receiver, where the pressure was released, and then passed through meters to be processed in the paraffin plant.

Adsorption of gasol and naphtha on activated charcoal. The adsorption plant was built in two construction periods. Plant I consisted of eleven adsorbers each with a capacity of 9 tons of charcoal. The adsorbers were cylindrical vessels (3.8 m diameter containing a bed of charcoal 1.8 m high) with dome-shaped tops and bottoms. The exit gas leaving the adsorbers was stripped of all hydrocarbons of molecular weight higher than that of propane and was used then for heating in the refinery and for steam production. The temperature of the adsorbers was kept below 40°C. After the charcoal had adsorbed 3–4 per cent of naphtha and 1–2 per cent of gasol ($C_3 + C_4$ hydrocarbons) by weight,

the gas stream was diverted into a fresh adsorber. The adsorbed hydrocarbons were stripped from the charcoal with steam and condensed with the steam in tubular condensers. The gasol thus separated from the naphtha and water was collected in a 1,000-cu-m gasholder and then compressed for further processing. The naphtha refining was done in the stabilization and distillation plants.

The steam-stripped adsorbers were first dried by heated recirculation gas which was then cooled for further gasol recovery. The charcoal was then cooled by further circulation of cool gas. The blowers for drying and cooling the charcoal had a capacity of 22,000 cu m per hr. The cycle, consisting of adsorption, stripping, drying, and cooling, was completed in from 24 to 60 minutes, depending on the load. The gas stream was controlled by hydraulically operated disc valves of 700-mm diameter. The hydraulic control operated automatically through time relays from a central switchboard in the control room. After gasol separation, the residual gas (CO_2, CO, H_2) was returned to the adsorber inlet.

Up to 1.5 per cent by weight of the charcoal, the naphtha adsorption efficiency was 100 per cent. At a naphtha content of 3–5 per cent by weight of the charcoal the gasol adsorption efficiency was 95 per cent. The guaranteed capacity of the charcoal, 1.25 kg of charcoal per ton of hydrocarbons, was actually exceeded. Usually the brand of charcoal known as Supersorbon F.S., in the form of pellets 4 mm diameter and 4 to 6 mm long, was used.

Plant II consisted of four adsorbers of 5.5-m diameter each containing 18 tons of charcoal in a 2.20-m depth. Instead of a separate circuit for cooling and drying, a series system was used in which the synthesis exit gas passed through all the adsorbers in series except the one which was stripped. Thirty-three thousand cubic meters per hour of gas passed

Table 20. Analyses of Entering and Exit Gases, Volume Per Cent, of Charcoal Adsorption Plant of Ruhrchemie, 1943–1944

	Gas from Atmospheric-Pressure Plant		Gas from Medium-Pressure Plant	
	Before Adsorption	After Adsorption	Before Adsorption	After Adsorption
CO_2	36.5	36.6	44.2	42.3
C_nH_m	1.3	0.5	2.0	0.5
CO	14.1	15.2	9.7	12.0
H_2	10.8	11.9	16.0	17.2
C_nH_{2n+2}	16.0	13.6	13.2	11.4
N_2	21.3	22.2	14.9	16.6
n in C_nH_{2n+2}	1.69	1.11	1.79	1.10

through the drying and cooling circuit. The condensation and separation equipment was installed as in plant I. Plant II included also a large direct-cooling tower to cool the drying and cooling gas. Gas analyses of the entering and exit gases of the charcoal adsorption plant are given in Table 20. These data are for the Ruhrchemie operations in 1943–1944.

Carbon dioxide was recovered from the residual gases in an "alkazid" plant and was used for flushing and fire-extinguishing purposes.

Additional data on composition of products from Sterkrade-Holten Plant. The composition of the primary liquid products from the cobalt-thoria-magnesia-kieselguhr catalyst employed in the Ruhrchemie process is shown in Table 21.[52] The product distribution data

Table 21. Composition of Liquid Products from Ruhrchemie Process

(Weight per cent of total oil product.)

Carbon Number of Fraction	Atmospheric-Pressure Synthesis	Middle-Pressure Synthesis
3	5	1.5
4	7	2.5
5	11.2	7.1
6	10.7	7.1
7	9.0	6.1
8	7.7	5.0
9	6.3	3.5
10	5.7	26.8
11–18	27.4	
Above 18	10.0	40.4

given in Table 10, Chapter 3, and Tables 3, 16, 17, 18, and 21 of this chapter exhibit some differences. Those of Table 10, Chapter 3, and Table 3 of this chapter are for earlier operations and laboratory tests made in the period 1936–1939, and those of Tables 16, 17, 18, and 21 are characteristic of the products obtained in 1943–1944.

The analysis by low-temperature distillation of the end gases (before passage through the activated-charcoal scrubbers) from the atmospheric- and medium-pressure plants and the results of some calculations based on these data [49] are shown in Table 22. The percentages of olefins in the C_2, C_3, and C_4 fractions are 9.9, 20.1, 43.1, respectively, for the atmospheric-pressure plant and 4.0, 11.3, 25.4, respectively, for the medium-pressure plant. The gasol recovery in the atmospheric-pressure plant was not as high as in the medium-pressure plant because of the appreciably lower concentration of the $C_3 + C_4$ fraction in the end gas of the lower-pressure plant. The medium-pressure plant produced more

[52] T.O.M. Reel 45, Bag 3,441, Item 76.

TABLE 22. ANALYSIS OF END GASES BY LOW-TEMPERATURE DISTILLATION

(Ruhrchemie Process; Sterkrade-Holten plant data for operation in November 1943.)

Low-Temperature Distillation Analyses of End Gases		
Constituent, volume per cent	Atmospheric-Pressure Plant	Medium-Pressure Plant
CO_2	43.50	33.40
CO	9.90	14.13
H_2	15.13	9.83
N_2	17.55	26.05
CH_4	8.87	11.39
C_2H_4	0.103	0.036
C_2H_6	0.940	0.871
C_3H_6	0.228	0.160
C_3H_8	0.905	1.255
C_4H_8	0.421	0.313
C_4H_{10}	0.557	0.919
C_5 and higher	1.970	1.918
Derived Data		
Item	Atmospheric-Pressure Plant	Medium-Pressure Plant
Gasol ($C_3 + C_4$), g per cu m of		
End gas	48.7	61.4
Synthesis gas	17.5	16.4
$CO + H_2$	22.0	19.1
Per cent of gasol recovered in charcoal plant		
	55.0	81.7
Per cent conversion of CO entering plant to		
CO_2	4.2	4.8
CH_4	10.6	8.8
C_2	2.8	2.0
$C_3 + C_4$	10.4	8.6
Oil	58.4	64.0
Total	86.4	88.2

oil and less methane and C_2 hydrocarbons than the atmospheric-pressure plant. Although the percentage of methane in the end gases is much higher than that of C_2 or C_3 hydrocarbons, the percentages of C_2, C_3, and C_4 hydrocarbons are about equal.

The isomeric composition of the C_5, C_6, C_7, and C_8 hydrocarbon fractions of the product from a cobalt-thoria-kieselguhr catalyst tested in a laboratory reactor at 190°C and atmospheric pressure of $2H_2 + 1CO$ gas has been reported by Friedel and Anderson [53] of the U. S. Bureau of Mines. The C_5–C_9 oil fraction was 37.8 volume per cent of the total oil product. The C_5–C_9 saturated hydrocarbon fraction was separated by adsorption on silica gel from the oxygenated material and the olefins, which were, respectively, 9.1 and 19.2 volume per cent of the C_5–C_9 oil fraction. The saturated hydrocarbons were fractionated by distillation into five fractions which were analyzed by mass spectrometric procedures. Table 23 contains the results. The comments of the authors [53] on this table are:

> Isomeric percentages are given for each fraction on the basis of 100 per cent. Of particular interest is the slight but progressive decrease of the straight-chain isomers, the major components, with molecular weight. . . . Calculated results are given in the table in parentheses for various ethyl- and dimethyl-derivatives. In all cases the percentages were very close to zero, being either slightly positive or negative. This is considered valid evidence for the absence of appreciable concentrations, but the difficulties of carrying out separations on a small scale did not allow precluding the presence of traces. In these calculations only one isomer containing a quaternary carbon atom, 2,2-dimethylbutane, was investigated, and this was found to be absent (−0.4 per cent).

The absence of branched hydrocarbons with more than one branch per molecule, and more than one carbon atom per branch, is of both theoretical and practical importance. As molecules with only a single branch consisting of a methyl group contribute little to the octane rating of the gasoline, compared with the contribution of more highly branched hydrocarbons and olefins, a suitable motor gasoline can be obtained directly from the synthesis only if the olefin content is quite high.

The impact of the analytical data is far-reaching so far as the mechanism of the synthesis is concerned. The presence of only very small amounts of multiply branched hydrocarbons, and of branches longer than a methyl group, shows that the probability of addition of carbon monoxide and hydrogen varies with the position of the double bond. A possible mechanism is that, after methylene groups are formed by reduction of chemisorbed carbon monoxide, ethyl alcohol is formed by re-

[53] R. A. Friedel and R. B. Anderson, Composition of Synthetic Liquid Fuels. I. Product Distribution and Analysis of C_5–C_8 Paraffin Isomers from Cobalt Catalyst, *J. Am. Chem. Soc.*, **72**, 1,212–5 (1950).

action of the methylene groups with carbon monoxide and hydrogen. Subsequent dehydration of this alcohol yields ethylene which reacts with carbon monoxide and hydrogen to form propyl alcohol. Repetition of this cycle results in production of higher-molecular-weight hydrocarbons. At various stages in this reaction chain, olefins are either desorbed as such or are hydrogenated to form saturated hydrocarbons.

Table 23. Isomeric Composition of C_5–C_8 Saturated Hydrocarbon Fractions

Component	Composition, volume per cent
n-Pentane	94.9
i-Pentane	5.1
n-Hexane	89.6
2-Methylpentane	5.8
3-Methylpentane	4.6
2,2-Dimethylbutane	(−0.4)
2,3-Dimethylbutane	(−0.04)
n-Heptane	87.7
2-Methylhexane	4.6
3-Methylhexane	7.7
3-Ethylpentane	(−0.7)
2,3-Dimethylpentane	(−0.02)
2,4-Dimethylpentane	(−0.6)
n-Octane	84.5
2-Methylheptane	3.9
3-Methylheptane	7.2
4-Methylheptane	4.4
3-Ethylhexane	(0.3)
2,3-Dimethylhexane	(Neg.) [a]
2,4-Dimethylhexane	(Neg.) [a]
2,5-Dimethylhexane	(Neg.) [a]

[a] No definite negative values could be calculated for these.

This mechanism is in accord with data on the quantitative analysis of the products and with data which show that alcohols actually are the precursors of the olefins in the synthesis (see below; sections on composition of products from end-gas-recycle operations). A more complete discussion of the mechanism of the synthesis is presented in Chapter 6.

Concerning the position of the double bond in the olefin fractions, Friedel and Anderson [53] state:

> Analyses for general olefin types in the C_6–C_8 range by infrared spectrometry revealed the predominance of internal double bond olefins over the alpha form. This predominance increased with molecular weight. Further, the "trans-" configuration was found in greater concentration than the "cis-" form of internal olefins.

The data are given in Table 24. The proportion of α-olefins was higher than would be predicted from thermodynamic equilibrium calculations.

Table 24. Types of Olefins in C_6–C_8 Fraction of Product from Cobalt-Thoria-Kieselguhr Catalyst

Fraction	Alpha-Olefins	Internal Double-Bond Olefins	
		trans-	*cis-*
	Volume Per Cent		
C_6	36	39	25
C_7	28	42	30
C_8	18	52	30

A vacuum distillation of Ruhrchemie's wax product was made at 10 mm pressure up to 380°C and at 0.6 mm from 380°C to 600°C. The results [21] are presented in Table 25.

Table 25. Vacuum Distillation of Wax at 10 mm to 380°C and at 0.6 mm from 380° to 600°C

Temperature, °C	180	200	220	240	260	280	300	320	340
Weight per cent	0.2	0.87	2.07	3.62	5.49	9.23	12.77	19.39	23.60
Temperature, °C	360	380	400	420	440	460	480	500	520
Weight per cent	33.84	43.20	45.07	50.59	56.97	63.68	67.38	71.65	77.56
Temperature, °C	540	560	580	600	Residue		Hold-up + loss		
Weight per cent	81.60	82.02	89.62	91.06	8.71		0.23		

No analyses of oil-soluble oxygenated compounds from cobalt catalyst are available except for operations employing end-gas recycle (see below). Data on the oxygenated organic compounds in the reaction water plus condensed steam from the charcoal adsorption plant from Ruhrchemie medium-pressure operations in 1943 show [54] that a total of 1.16 kg of alcohols is produced per metric ton of C_3+ oil. This amounts to about 0.18 g of water-soluble material per cu m of $CO + H_2$, as compared with about 13.8 g of oil-soluble organic compounds. The water-soluble alcohols consisted of about 10 per cent CH_3OH, 15 per cent C_2H_5OH, 20 per cent C_3H_7OH, and 40 per cent of C_4–C_6 alcohols. Much smaller amounts of fatty acids, esters, and aldehydes were present.

[54] T.O.M. Reel 45, Bag 3,441, Item 79.

Only in the Hoesch-Benzin plant were water-soluble alcohols and fatty acids regularly recovered.[50] Aqueous liquor comprising the reaction water separated from the oil after the product condensers, plus the condensed water from steaming the active charcoal scrubbers, was distilled. The original concentration of alcohols was 0.5 per cent by weight. After distillation, the concentration of organic matter was 70 per cent, 8–10 per cent of which was aldehydes, ketones, and esters. The remainder was a mixture of alcohols, namely, 10 per cent methyl, 25 per cent ethyl, 30 per cent propyl, 25 per cent butyl, and 10 per cent amyl and hexyl alcohols. The alcohols recovered amounted to about 0.6 per cent of the total primary products and about 45 per cent of the total water-soluble organic matter. No recovery of oil-soluble alcohols was made.

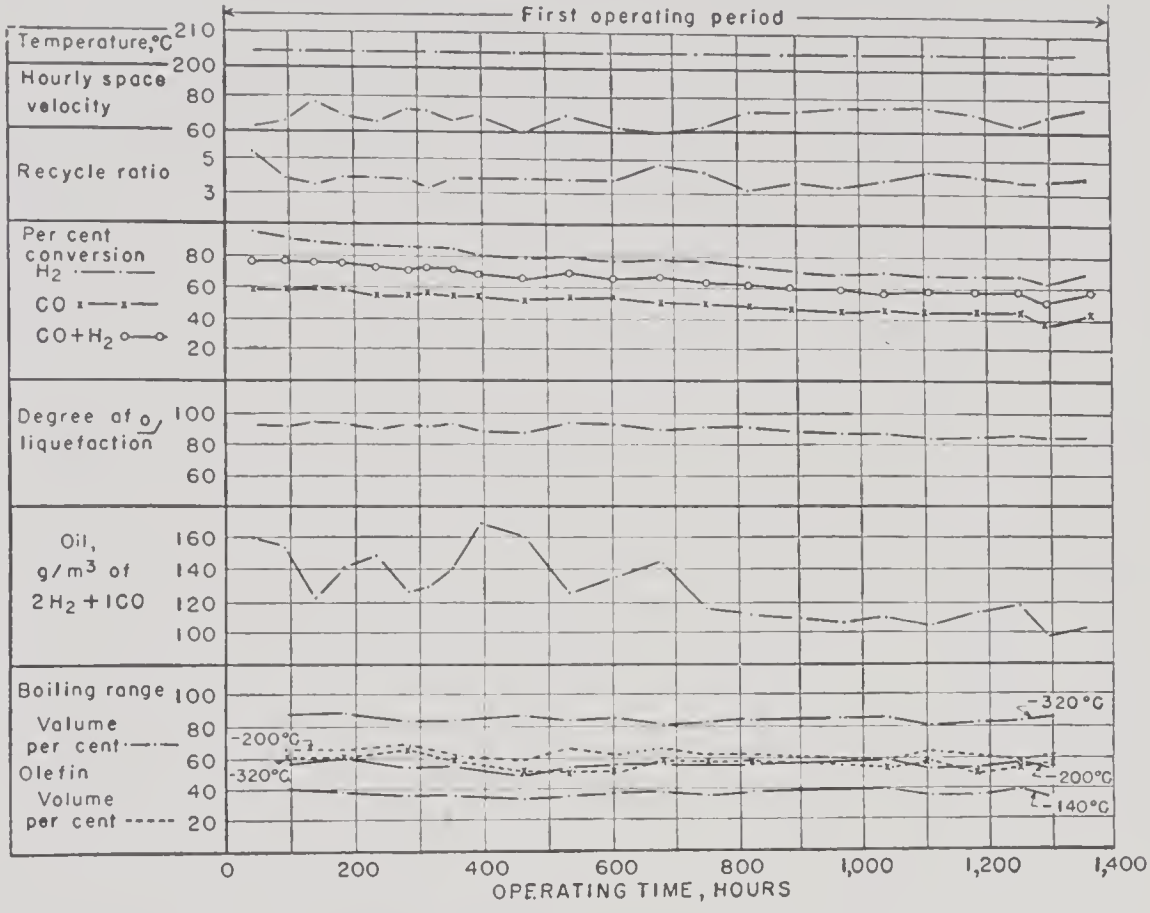
Fatty acids were recovered at the Hoesch plant by neutralization with soda solution of the hot gases from the reactors, and by scrubbing the Diesel oil fraction of the product with soda solution. The combined soda solutions were acidified with sulfuric acid, and the liberated fatty acids extracted with benzol. The recovered acids contained 30 per cent of C_2–C_4, 30 per cent of C_5–C_9, 35 per cent of C_{10}–C_{20}, and 5 per cent of higher fatty acids. The recovered fatty acids amounted to 0.4 per cent of the total primary products or about 30 per cent of the total water-soluble organic matter.

PROCESSES RECYCLING END GAS THROUGH GRANULAR, FIXED BEDS OF CATALYST, COOLED BY INDIRECT HEAT EXCHANGE

Lurgi Experiments with a Diluted Cobalt Catalyst

Since 1935 it was known that in the Ruhrchemie process most of the synthesis occurs in the middle portion of the catalyst.[55, 56] This results in uneven distribution of the heat of reaction and makes precise temperature control difficult. In 1938–1939 Lurgi (Gesellschaft für Wärmetechnik, Hidernheim near Frankfurt-am-Main) investigated the effect of recycling 1–5 volumes of end gas per volume of fresh gas, using a "diluted" cobalt-thoria-magnesia-kieselguhr catalyst containing 3 times as much kieselguhr as the normal Ruhrchemie catalyst. Although originally designed to improve the efficiency of the Ruhrchemie process, the main objective of the research shifted quickly towards the production of a

[55] T.O.M. Reel 45, Bag 3,441, Items 85 and 88.
[56] T.O.M. Reel 35, Bag 3,452, Item 4-c.



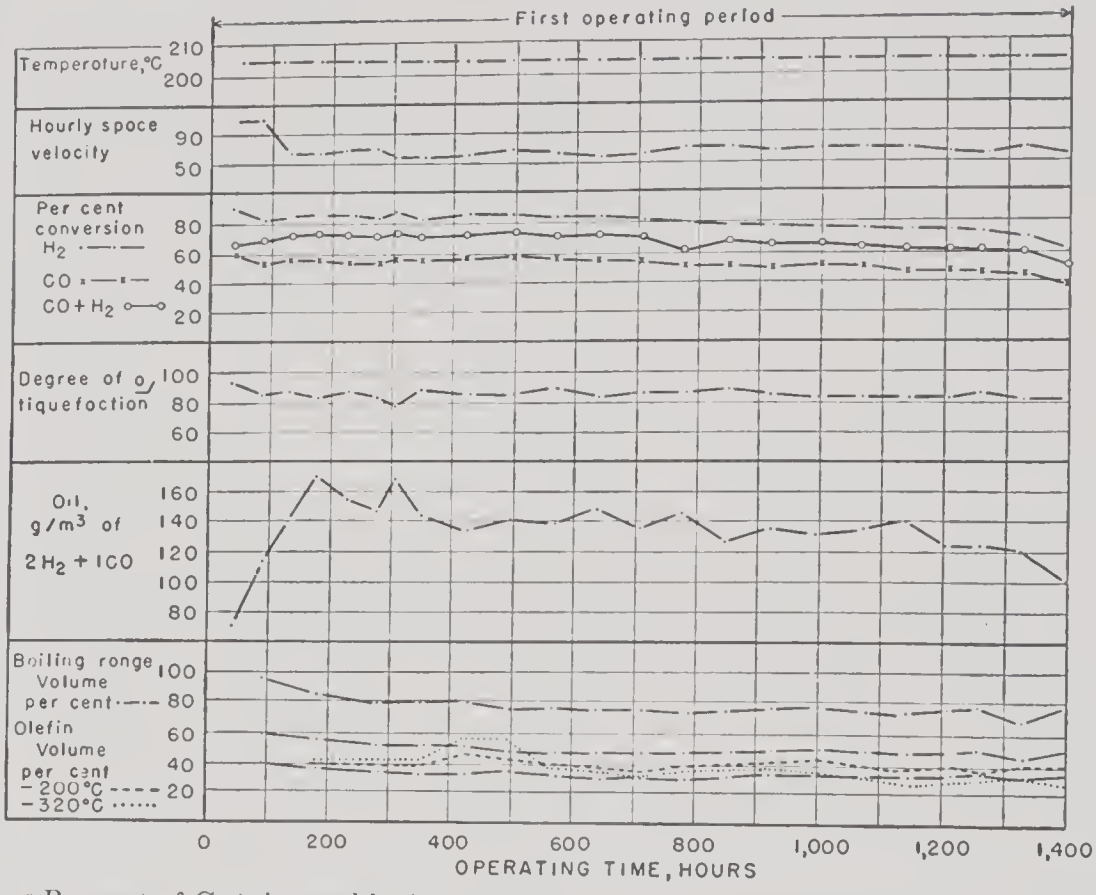
[a] Per cent of C_3+ in total hydrocarbons.

FIGURE 4–7. Extruded cobalt-thorium-magnesium-kieselguhr catalyst (100:5:10:600) with water gas and recycle. Reproduced from reference 57.

maximum yield of olefins to supply a more satisfactory raw material for the synthetic lubricating oil and oxo processes.

Dilution of the catalyst with kieselguhr and dilution of water gas ($1.3H_2 + 1CO$) with recycled end gas so as to lower the partial pressure of CO resulted in a higher olefin content of the products without the excessive carbon deposition and the more rapid catalyst deterioration normally associated with the use of water gas. The Lurgi tests [57] were done with $100Co:5ThO_2:10MgO:600$ kieselguhr catalysts, in single externally cooled tubes. During the first test period, September 9 to November 6, 1938, the operating temperature and pressure were, respectively, 205°C and 7 atm, and the space velocity per hour of fresh gas was 70. Average gas analyses for this 8-week period are shown in Table 26. The operating and yield data are given in Figures 7, 8, 9, and 10. Figures 7 and 8 contain operating and yield data for tubes 1 with recycle and 2 without recycle, respectively, of Table 26.

[57] T.O.M. Reel 47, Bag 3,446, Item 96.



[a] Per cent of C_3+ in total hydrocarbons.

FIGURE 4–8. Extruded cobalt-thorium-magnesium-kieselguhr catalyst (100:5:10:600) with water gas without recycle. Reproduced from reference 57.

TABLE 26. LURGI RECYCLE TESTS, USING WATER GAS AND DILUTED COBALT CATALYST, FIRST OPERATING PERIOD OF 8 WEEKS

	Gas Analyses, volume per cent			
			Tail Gases	
Constituent	Fresh Gas	Recycle Gas	Tube 1 with Recycle	Tube 2 without Recycle
CO_2	0.3	1.3	1.4	2.2
C_nH_m	0.0	0.1	0.1	0.6
CO	39.0	44.6	44.3	45.2
H_2	50.1	29.3	26.9	22.8
CH_4	0.2	3.0	3.5	4.3
N_2	10.3	21.5	23.6	24.7
n	....	1.03	1.04	1.23

Figures 9 and 10 show more clearly the product distributions obtained with and without recycle. The results may be summarized by stating that the diluted catalyst operating on water gas without recycle gives

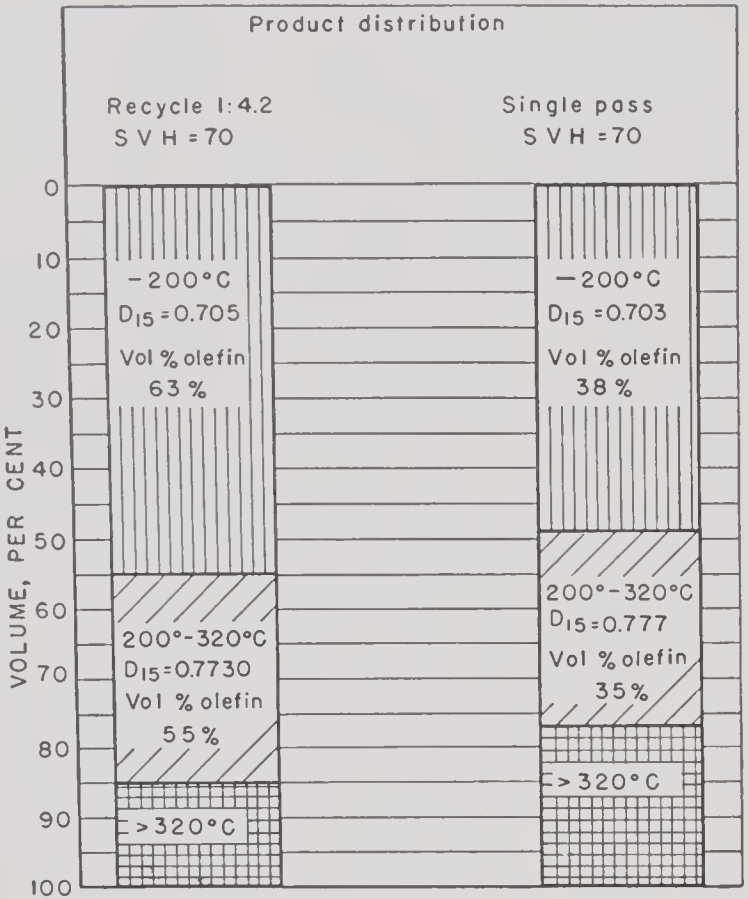


FIGURE 4–9. Extruded cobalt catalyst (100Co:5ThO_2:10MgO:600 kieselguhr) in water-gas operation with and without recycle. Reproduced from reference 57.

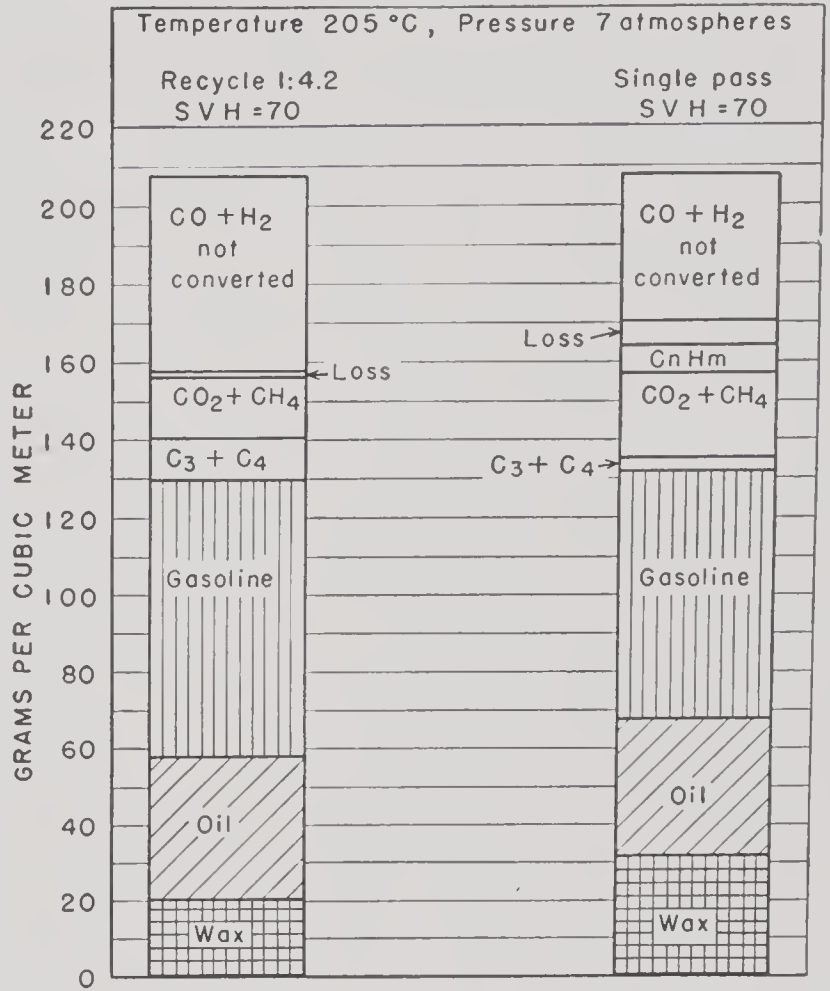
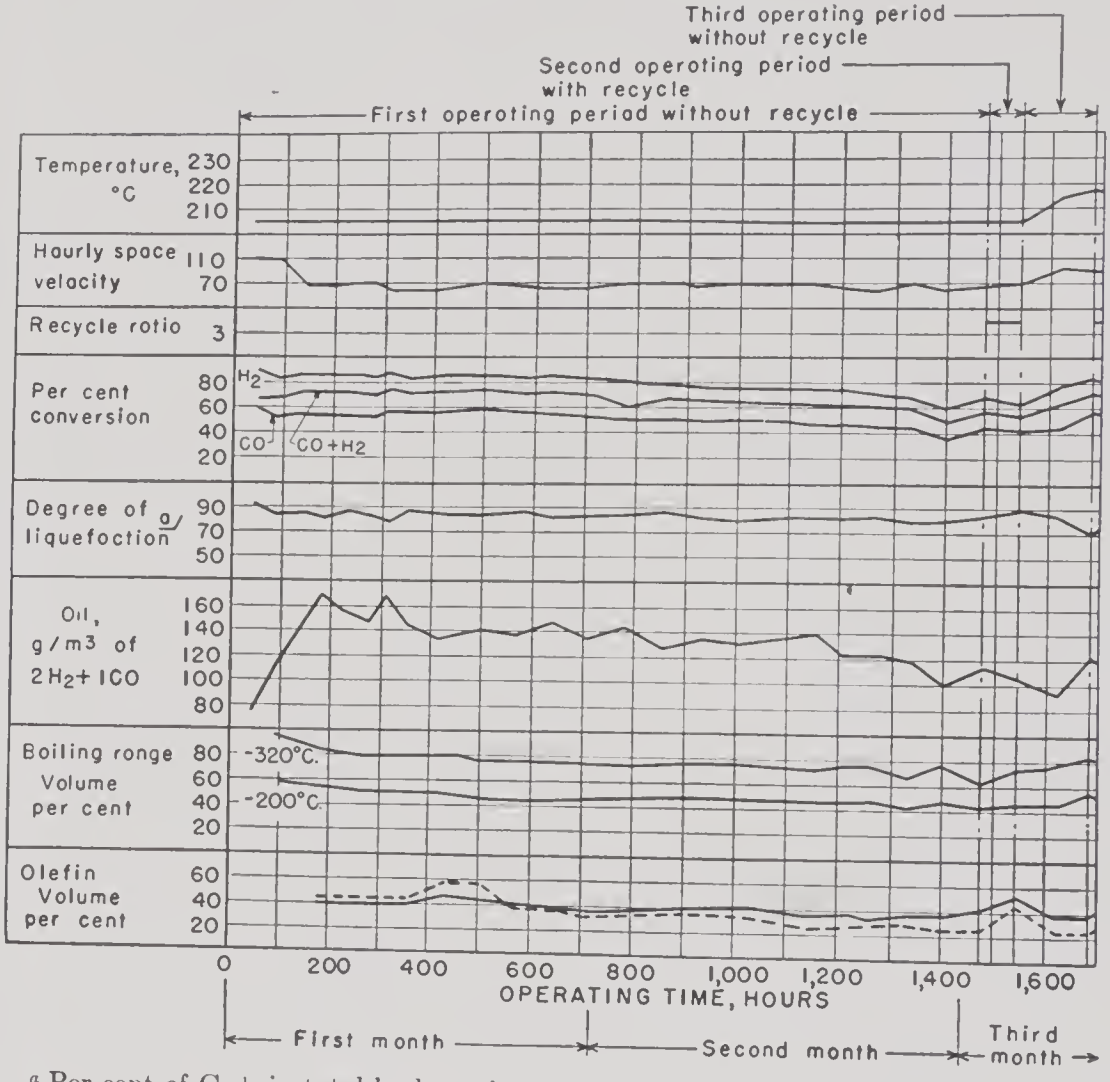


FIGURE 4–10. Extruded cobalt catalyst (100Co:5ThO_2:10MgO:600 kieselguhr) in water-gas operation with and without recycle. CO balance for 8 weeks. Reproduced from reference 57.

about the same yield as the denser normal Ruhrchemie catalyst operating on $2H_2 + 1CO$. The diluted catalyst operating on water gas with recycle of about 4 volumes of end gas per volume of fresh gas produces less



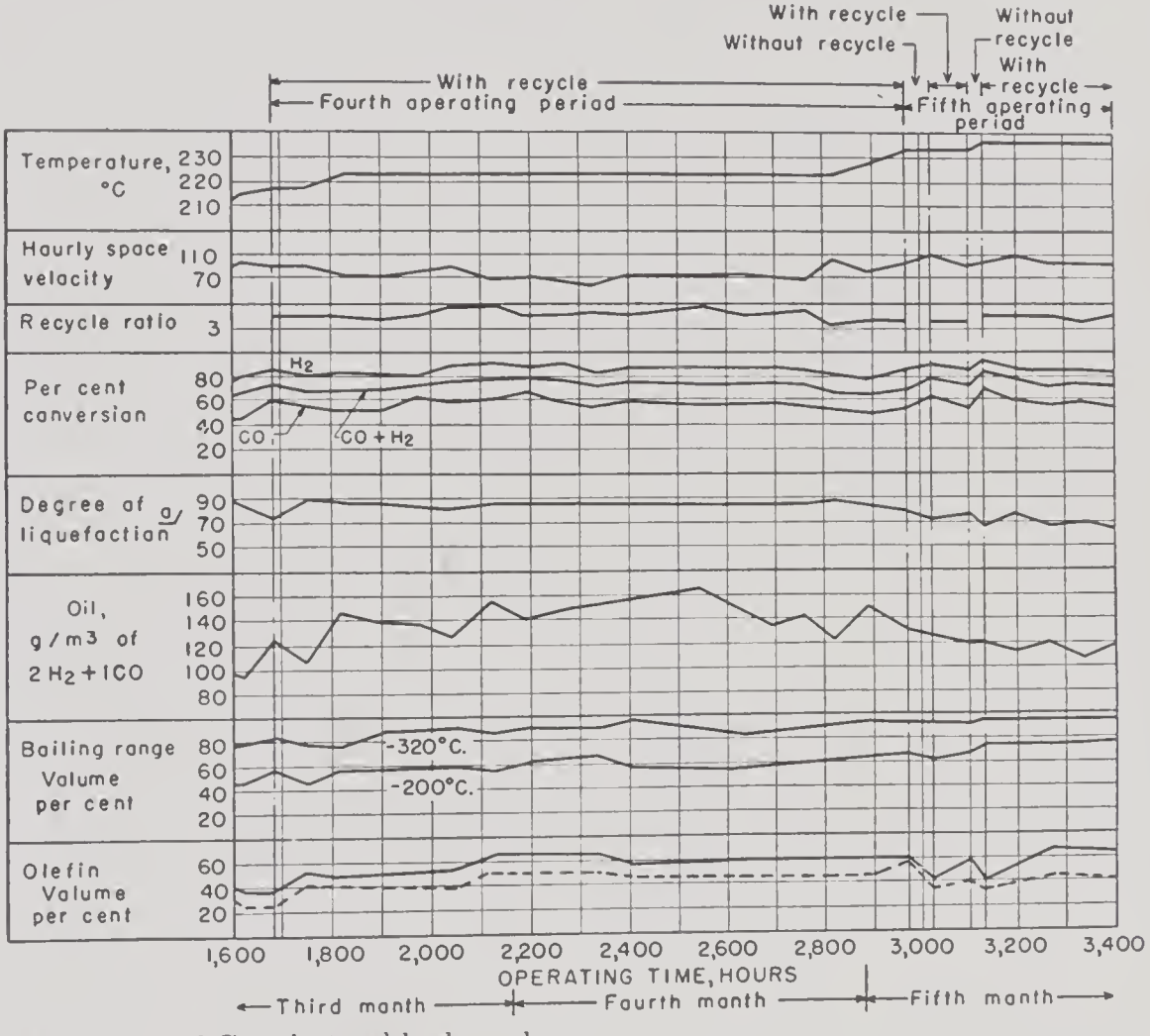
[a] Per cent of C_3+ in total hydrocarbons.

FIGURE 4–11. Diluted cobalt-thorium-magnesium-kieselguhr catalyst (100:5:10:600), 14 per cent Co, with water gas with and without recycle. Reproduced from reference 57.

methane and about 6 per cent more of oil of much higher olefin content than when operating on the same gas without recycle.

In the second operating period from November 12 to November 15, 1938, tube 2, which had been on stream without recycle for 8 weeks, was run with recycling. The conversions and yields were virtually identical with those for tube 1 during the first period. For purposes of continuity the data of Figure 8 for tube 2, first period, are reproduced in Figure 11, which includes also the third operating period.

In the third and fourth operating periods from November 15, 1938, to January 14, 1939, the temperature was increased to restore the conversion to the same value as at the start of the first period. In the first and second periods the temperature was kept constant at 205°C. The hydrogen conversion dropped during this interval from 85 to 70 per cent.



[a] Per cent of C_3+ in total hydrocarbons.

FIGURE 4–12. Diluted cobalt-thorium-magnesium-kieselguhr catalyst (100:5:10:600), 14 per cent Co, with water gas with and without recycle. Reproduced from reference 57.

In the third period tube 2 was run without recycle. To attain 85 per cent hydrogen conversion it was necessary to raise the temperature to 223°C, but the degree of liquefaction (per cent of C_3+ in total hydrocarbon product) dropped from 90 to 74 per cent. For normal Ruhrchemie operation without recycle, this catalyst would then have been discarded. Upon restoring the recycle in the fourth operating period, however, the degree of liquefaction rose to 85 per cent and operation was continued for 55 days. Average gas analyses for this 55-day period are shown in Table 27, and operating and yield data in Figure 12.

TABLE 27. LURGI RECYCLE TESTS, USING WATER GAS AND DILUTED COBALT CATALYST, FOURTH OPERATING PERIOD OF 55 DAYS

Constituent	Gas Analyses, volume per cent		
	Fresh Gas	Recycle Gas	Tail Gas
CO_2	2.1	5.2	6.1
C_nH_m	0.0	0.2	0.3
CO	38.7	44.1	45.0
H_2	51.0	26.3	21.3
CH_4	0.3	4.7	5.8
N_2	7.8	19.1	21.6
n	....	1.02	1.03

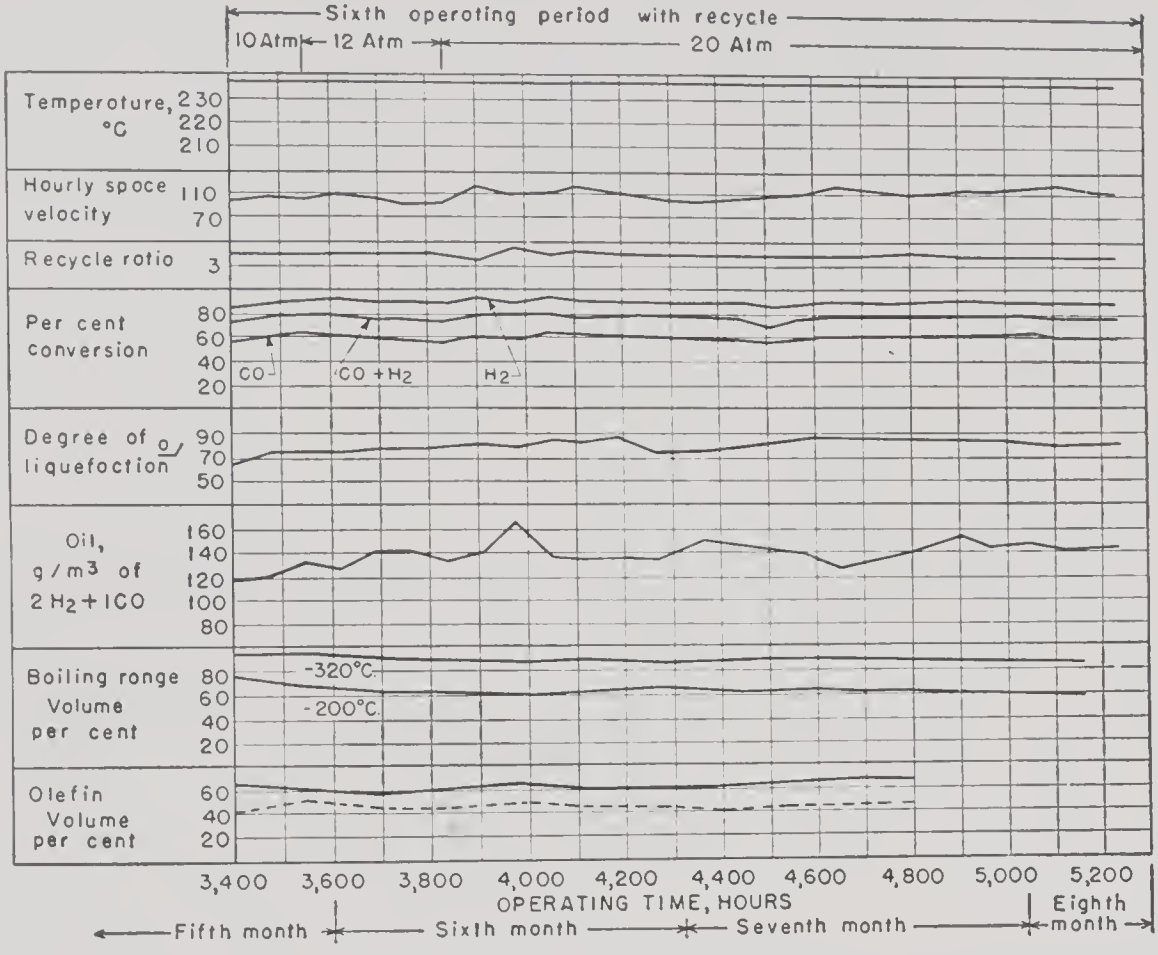
In the fifth operating period (see Figure 12) the space velocity of fresh gas was increased from 70 to 100 per hr, which necessitated an increase in temperature to 233°C to maintain constant conversion, but the degree of liquefaction dropped from 87 to 79 per cent. Recycling was stopped, whereupon the degree of liquefaction dropped to 72 per cent. Restoration of the recycle did not improve the liquefaction; and after the recycling was again stopped, the temperature was increased to 237°C. The degree of liquefaction dropped further to 67 per cent and did not improve upon restoring the recycle. It was concluded, therefore, that no increase in space velocity was possible after about 3,000 hr of operation.

During the sixth operating period (1,800 hr; see Figure 13 for operating data and yield and Table 28 for gas analyses) the pressure was increased

TABLE 28. LURGI RECYCLE TESTS, USING WATER GAS AND DILUTED COBALT CATALYST, SIXTH OPERATING PERIOD OF ABOUT 75 DAYS

Constituent	Gas Analyses, volume per cent		
	Fresh Gas	Recycle Gas	Tail Gas
CO_2	7.1	15.8	18.3
C_nH_m	0.0	0.6	0.4
CO	35.4	36.4	36.4
H_2	47.2	18.3	13.3
CH_4	0.5	6.3	7.0
N_2	9.6	22.5	24.5
n	....	1.15	1.12

to 20 atm. More than 2 months of satisfactory operation was obtained. The space velocity per hour of fresh gas was 70 and 4 volumes of end gas per volume of fresh gas were recycled. The total operating time, periods 1–6 inclusive, was $7\frac{1}{2}$ months with an average yield of 130 g of oil per cu m of ideal gas. Lurgi concluded that the life of the diluted catalyst operating on water gas exceeds that of the normal Ruhrchemie cobalt



[a] Per cent of C_3+ in total hydrocarbons.

FIGURE 4–13. Diluted cobalt-thorium-magnesium-kieselguhr catalyst (100:5:10:600), 14 per cent Co, with water gas and recycle. Reproduced from reference 57.

catalyst operating on $2H_2 + 1CO$, and suggested that the tail gases from recycle operation on diluted cobalt could be used as feed gas for an iron catalyst, in view of the relatively high carbon monoxide content.

RUHRCHEMIE PILOT-PLANT RECYCLE OPERATIONS WITH COBALT CATALYST

In the Ruhrchemie's pilot-plant tests on recycling of end gas the standard $100Co:5ThO_2:8MgO:200$ kieselguhr catalysts was used. Tests were made at atmospheric and at 7–10 atm of water gas ($1.3H_2 + 1CO$) plus recycle gas. Data for the atmospheric-pressure tests are shown in Table 29.[58] The data show an increase of the fraction of carbon monoxide converted to oil and of the olefin content of the oil with increasing recycle ratio. The yields of oil and gasol in the 3.1 recycle ratio test were, respectively, 95 and 9.2 g per cu m of inert free fresh gas, and the

[58] T.O.M. Reel 37, Bag 3,451, Item 21.

TABLE 29. RUHRCHEMIE PILOT-PLANT TESTS ON RECYCLING END GAS AT ATMOSPHERIC PRESSURE OVER 100Co:5ThO_2:8MgO:200 KIESELGUHR CATALYST, SEPTEMBER 1940 TO FEBRUARY 1941

Reactor, charge number	2, 8			2, 8			9, 3		
kg of catalyst	41			41			32		
Duration of test, hr [a]	121			112			743		
Space velocity per hr	110			107			145		
Temperature, °C	193			198			194–205		
Recycle ratio [b]	0.5			2.75			3.1		
Gas analyses, volume per cent:	Fresh	End	Recycle	Fresh	End	Recycle	Fresh	End	Recycle
CO_2	6.8	12.2	8.6	6.7	14.1	12.1	7.0	14.1	12.3
C_nH_m	0.0	0.5	0.4	0.0	0.7	0.6	0.0	0.4	0.3
CO	38.0	39.2	38.4	38.0	40.6	39.9	37.8	41.2	40.4
H_2	48.8	34.5	42.8	48.1	28.2	33.3	48.9	29.9	34.4
CH_4	0.3	2.6	1.2	0.3	3.4	2.8	0.3	3.1	2.4
N_2	6.0	10.9	8.5	6.6	12.9	11.2	5.9	11.5	10.1
n	....	1.10	1.05	..	1.13	1.11	....	1.05	1.03
Use ratio, H_2:CO	1.92			1.92			1.96		
Contraction, per cent	40.8			50.0			50.4		
Per cent conversion of	CO	H_2	CO+H_2	CO	H_2	CO+H_2	CO	H_2	CO+H_2
To total products	39.9	58.2	49.8	46.8	70.7	60.4	46.0	69.7	59.4
To oil	31.8	22.4	26.5	38.9	26.9	32.2	40.8	27.6	33.3
CO converted to	CH_4	CO_2		CH_4	CO_2		CH_4	CO_2	
As per cent of CO reacted	15.4	2.8		15.4	2.0		11.5	0.0	
Olefins + oxygen compounds in	Gasoline	Diesel oil		Gasoline	Diesel oil		Gasoline	Diesel oil	
Volume, per cent	45	16		55	36		67	45	

[a] Volumes of fresh gas per volume of catalyst per hour. [b] Volumes of end gas per volume of fresh gas in feed.

TABLE 30. ANALYSES OF COBALT CATALYSTS USED IN RUHRCHEMIE PILOT-PLANT RECYCLE OPERATIONS WITH WATER GAS

Charge number	22	24	25	26
Analysis before reduction, weight per cent				
Cobalt	24.00	23.65	22.66	19.90
Thoria	1.25	1.18	1.17	.....
Magnesia	1.84	1.84	1.80	.....
Kieselguhr	42.83	48.03	47.80	48.44
Analysis after reduction, weight per cent				
Cobalt	31.8	31.2	29.9	26.34
Thoria	.....	1.56	1.54	.....
Magnesia	.....	2.34	2.38	.....
Per cent reduction	45	50	55	42
Bulk density	0.282	0.285	0.251	0.259
Dust content, weight per cent	1.4	1.3	0.7	0.3
Weight ratios				
Cobalt	100	100	100	100
Thoria	5.2	4.98	5.17	...
Magnesia	7.64	7.78	7.95	...
Kieselguhr	179	203	210	243

TABLE 31. RUHRCHEMIE RECYCLE PILOT-PLANT DATA FOR 7 ATM OPERATION IN PERIOD OCT. 29 TO NOV. 11, 1942: TEST

Time, months	1			2			3		
Fresh gas, space velocity per hr	134			124			121		
Recycle ratio	2.46			3.14			3.09		
Temperature, °C	203.8			206.6			210.7		
Gas analyses, volume per cent	Fresh	End	Recycle	Fresh	End	Recycle	Fresh	End	Recycle
CO_2	5.7	13.2	11.0	5.8	13.1	11.3	6.0	13.8	11.9
C_nH_m	0.0	0.7	0.5	0.0	0.7	0.5	0.0	0.7	0.5
CO	39.8	45.2	43.6	39.3	44.6	43.3	39.2	44.5	43.2
H_2	48.3	24.5	31.4	48.4	25.2	30.8	48.0	23.2	29.3
CH_4	0.3	3.0	2.2	0.3	3.4	2.7	0.3	3.9	3.0
N_2	5.8	13.3	11.2	6.1	12.9	11.3	6.4	13.8	12.0
n	....	1.21	1.15	...	1.23	1.17	...	1.26	1.20
Per cent conversion of	Total	To oil		Total	To oil		Total	To oil	
$CO + H_2$	65.6	55.8		62.6	56.1		64.7	55.2	
CO converted to	CH_4	CO_2		CH_4	CO_2		CH_4	CO_2	
Per cent of CO reacted	5.0	0.2		7.1	1.8		7.9	1.4	
Yield of	C_5+	$C_3 + C_4$		C_5+	$C_3 + C_4$		C_5+	$C_3 + C_4$	
g per cu m of $CO+H_2$	101	14		97	14		99	14	
Boiling range, °C	To 200	200–320		To 200	200–320		To 200	200–320	
Weight per cent	48.6	20.4		52.2	25.6		52.6	26.4	
Boiling range, °C	320–460	Above 460		320–460	Above 460		320–460	Above 460	
Weight per cent	21.4	9.6		17.0	5.2		16.1	4.9	
Boiling range, °C	To 200	200–320		To 200	200–320		To 200	200–320	
Olefins + oxygen compounds, volume per cent	61.5	44.5		62.0	42.7		59.5	42.0	
Synthetic lubricating oil									
Weight per cent of 60°–200°	41.5			42.4			38.5		
Weight per cent of C_3+	15.5			16.9			15.5		
Viscosity, 50°C	11.0			10.7			9.1		
Viscosity, pole height	1.66			1.71			1.76		
Space-time conversion, cu m of $CO + H_2$ per cu m of catalyst per hr	77.5			68.2			68.9		

product distribution was 60 per cent gasoline (to 200°C), 26 per cent Diesel oil (200°–320°C), and 12 per cent wax (above 320°C). This product distribution is not significantly different from that for the atmospheric-pressure plant using $2H_2 + 1CO$ without recycle.

The Ruhrchemie made an exhaustive investigation of recycle operation with water gas at 7 atm. Pilot-plant operations usually were conducted in an experimental medium-pressure reactor containing 85 double tubes, 44 and 24 mm diameter, 4 m long. This reactor was charged with about 350 l of the standard Co-ThO_2-MgO-kieselguhr catalyst. A typical run (reactor No. 10, charge 22) is described in some detail.[59] The objective

[59] T.O.M. Reel 36, Bag 3,451, Item 1.

REACTOR NO. 10, CHARGE 22; MONTHLY AVERAGES FOR 6 MONTHS' RUN. INDUCTION PERIOD NOV. 11, 1942, TO MAY 11, 1943

4			5			6			Average 1 to 6		
120			113			101			119		
2.92			3.00			3.00			2.93		
214.0			217.7			223.2			213		
Fresh	End	Recycle	Fresh	End	Recycle	Fresh	End	Recycle	Fresh	End	Recycle
5.6	13.2	11.3	6.1	13.7	11.8	6.0	12.8	11.1	5.9	13.3	11.4
0.0	0.8	0.6	0.0	0.8	0.6	0.0	0.6	0.5	0.0	0.7	0.5
39.8	45.0	43.6	39.1	42.6	41.8	38.9	41.2	40.6	39.3	43.9	42.7
48.6	25.0	31.0	48.9	26.1	31.8	48.2	27.2	32.4	48.4	25.2	31.2
0.3	4.5	3.4	0.3	5.4	4.1	0.3	5.8	4.5	0.3	4.3	3.3
5.6	11.5	10.0	5.5	11.3	9.9	6.5	12.3	10.8	6.0	12.5	10.8
....	1.21	1.16	....	1.24	1.18	....	1.17	1.15	....	1.22	1.17
Total	To oil		Total	To oil		Total	To oil		Total	To oil	
63.4	53.5		62.1	51.3		58.6	49.3		63.0	53.5	
CH_4	CO_2		CH_4	CO_2		CH_4	CO_2		CH_4	CO_2	
9.4	2.7		12.6	2.9		15.1	3.9		9.5	2.0	
C_5+	$C_3 + C_4$		C_5+	$C_3 + C_4$		C_5+	$C_3 + C_4$		C_5+	$C_3 + C_4$	
92	15		84	17		68	23		90	16	
To 200	200–320		To 200	200–320		To 200	200–320		To 200	200–320	
56.1	24.4		57.6	26.0		67.6	24.3		55.8	24.5	
320–460	Above 460		320–460	Above 460		320–460	Above 460		320–460	Above 460	
16.0	3.5		13.0	3.4		6.4	1.7		15.0	4.7	
To 200	200–320		To 200	200–320		To 200	200–320		To 200	200–320	
58.5	40.3		55.6	40.0		53.8	34.2		60.2	40.6	
35.5			30.4			30.1			36.4		
15.1			12.7			13.4			14.8		
9.3			8.9			9.0			9.7		
1.82			1.83			1.92			1.78		
66.8			61.8			52.1			66.0		

was to operate for 6 months with recycle, using water gas. The analysis of the catalyst before and after reduction is given in Table 30, which contains similar data for charges 24, 25, and 26. The average data for 6 months of operation with each of charges 22, 24, 25, and 26 are given in Table 32. Table 31 contains more detailed data on operation with charge 22.

Reduced charge 22 was put into reactor No. 10 on October 29, 1942. The pilot plant was flushed at atmospheric pressure with end gas from the first stage of a standard full-scale Ruhrchemie plant, and then the temperature was raised to 167°C during 3 days of flow of end gas. The temperature was then lowered to 120°C, flow of water gas was started,

TABLE 32. RUHRCHEMIE RECYCLE PILOT-PLANT DATA FOR 7 ATM OPERATION IN REACTOR NO. 10, CHARGES 22, 24, 25, AND 26; COMPARISON OF RESULTS DURING FIRST MONTH OF OPERATION

Charge number	22			24			25			26		
Date	Nov.–Dec. 1942			Jan.–Feb. 1944			Mar.–Apr. 1944			May–June 1944		
Test period, hr	337–1,038			0–523			0–876			0–869		
Fresh gas, space velocity per hr	134			95			99			96		
Recycle ratio	2.46			2.96			2.89			3.01		
Temperature, °C	203–206			195.4			200.4			200.4		
Gas analyses, volume per cent	Fresh	End	Recycle	Fresh	End	Recycle	Fresh	End	Recycle	Fresh	End	Recycle
CO_2	5.7	13.2	11.0	6.3	13.3	11.5	6.6	14.1	11.5	6.5	17.2	14.4
C_nH_m	0.0	0.7	0.5	0.0	0.6	0.3	0.0	0.5	0.3	0.0	0.3	0.2
CO	39.8	45.2	43.6	39.8	43.7	42.6	38.6	42.6	41.2	38.4	44.7	43.4
H_2	48.3	24.5	31.4	49.6	30.1	35.4	49.4	29.6	36.4	50.0	23.4	30.0
CH_4	0.3	3.0	2.2	0.3	2.8	2.2	0.3	3.2	2.2	0.3	2.5	1.9
N_2	5.8	13.3	11.2	4.8	9.4	8.2	5.0	10.0	8.2	4.7	11.8	10.0
n	....	1.21	1.15	....	1.14	....	....	1.06	....	....	1.01	....
Use ratio, H_2:CO	1.87			2.05			1.99			1.95		
Conversion of	CO	H_2	CO+H_2	CO	H_2	CO+H_2	CO	H_2	CO+H_2	CO	H_2	CO+H_2
Per cent	50.5	77.8	65.6	41.2	66.2	53.7	45.2	70.0	57.6	54.4	81.6	68.0
Conversion of CO to	CH_4		CO_2	CH_4		CO_2	CH_4		CO_2	CH_4		CO_2
Per cent of CO reacted	5.0		0.2	7.2		4.1	7.4		2.2	3.3		1.2
Yield of	C_5+		$C_3 + C_4$	C_5+		$C_3 + C_4$	C_5+		$C_3 + C_4$	C_5+		$C_3 + C_4$
g per cu m of CO + H_2	101		14	79		.....	82		12	122		6
Boiling range, °C	To 200		200–320	To 200		200–320	To 200		200–320	To 200		200–320
Weight per cent	48.6		20.4	39.2		28.9	48.0		24.7	31.7		23.7
Boiling range, °C	320–460		Above 460	320–460		Above 460	320–460		Above 460	320–460		Above 460
Weight per cent	21.4		9.6	19.7		12.1	19.2		8.2	25.1		19.8
Boiling range, °C	To 200		200–320	To 200		200–320	To 200		200–320	To 200		200–320
Olefins + oxygen compounds, volume per cent	61.5		44.5	62		42	60		41	66		44
Diesel oil												
Pour point, °C	....			− 9.0			−12.0			− 9.0		
Cetane number	....			90.5			84.0			82.0		
Hard wax (>460°C)												
Melting point, °C	....			86			86			86		
Synthetic lubricating oil												
Weight per cent of 60°–200°C	41.5			45.3			40.8			45.5		
Weight per cent of C_3+	15.5			13.6			14.9			12.0		
Viscosity, 50°C	11.0			12.1			10.5			9.06		
Viscosity, pole height	1.66			1.65			1.65			1.61		
Space-time conversion, cu m of CO + H_2 per cu m of catalyst per hr	77.5			45.2			50.1			57.8		

and the pressure increased to 7 atm. Recycling was started simultaneously with the introduction of water gas. The initial space velocity of water gas was about 25 per hour. The temperature was raised to 181°C. This resulted in a 70 per cent conversion of CO + H_2. During the next 3 days the space velocity of water gas was increased to 50 per hour and the temperature to 190°C. In the following 3 days the space velocity of water gas was increased to 100 per hour and the temperature to 198.5°C; finally during the succeeding 2 days the space velocity of water gas was raised to 137 per hour, and the temperature to 203°C. After the induction period, which totaled 336 hr, the 6 months' test period was started. The space velocity of water gas was held at 134 per hour during the first month and gradually reduced to 101 per hour during the next 5 months. At the same time the temperature was progressively increased so as to maintain a conversion of 62–64 per cent of the CO + H_2 entering the reactor.

The data in Table 31 for operation with charge 22 indicate a progressive decrease in space-time-yield from 77 cu m of CO + H_2 converted per cu m of catalyst per hr in the first month to 52 cu m per hr in the sixth month. At the same time the methane yield increased from 5 per cent of the CO reacted in the first month to 15 per cent in the sixth month. Concomitant changes occurred in product distribution, olefin content, and in yield and quality of synthetic lubricating oil manufactured by polymerization of the gasoline fraction olefins.

The data in Table 32 [60] indicate the reproducibility of pilot-plant recycle operations. At approximately constant space velocity (95–99 per hour for charges 24, 25, and 26) and constant recycle ratio (2.89–3.01) the yield of oil and gasol, the product distribution, the olefin content of the gasoline, the yield and quality of the lubricating oil made by polymerization of olefins in the 60°–200°C fraction, and the quality of the Diesel oil vary appreciably without any obvious correlation with temperature. Possibly the differences in catalyst composition and per cent of reduction of catalyst (see Table 30) were sufficient to account for these variations in yield and quality of products.

Some details of composition of the gasoline fraction of the product from charge 26 are given in Table 33.[60] The high olefin content is characteristic of recycle operation products. Otherwise these gasoline analyses are about the same as those for gasoline from the medium-pressure synthesis without recycle.

The effect of space velocity of fresh gas on the recycle operation is shown by the data in Table 34.[59] With increasing space velocity from 80 to 119 per hour the specific yield (grams of oil per cubic meter of fresh

[60] T.O.M. Reel 37, Bag 3,450, Item 3.

TABLE 33. RUHRCHEMIE RECYCLE OPERATION, COMPOSITION OF GASOLINE FRACTION REACTOR 10, CHARGE 26

Component	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	Above C_{10}
Test period, hr	182–374							
Weight per cent of gasoline	1.6	10.2	12.3	15.2	16.5	18.4	14.7	11.1
Olefins + oxygen compounds, volume per cent of fraction	80.3	....	81.0	73.4	74.5	70.0	61.0	....
Test period, hr	896–1,035							
Weight per cent of gasoline	2.4	12.7	8.2	17.1	17.2	19.1	19.8	3.5
Olefins + oxygen compounds, volume per cent of fraction	....	77.5	70.5	63.5	62.5	56.0	45.5	....

gas) decreases but the space-time conversion (cubic meters of $CO + H_2$ converted per cubic meter of catalyst per hour) increases. With increasing space velocity the fraction of gasoline in the oil product increases and a corresponding decrease is observed in the fraction boiling above 320°C. Although the olefin content decreases only slightly in going from 80 to 120 space velocity per hour, the yield and quality of lubricating oil made by polymerization of the olefins in the 60°–200°C fraction decrease markedly. Possibly the degree of isomerization involving a shift in position of the olefin bond changes sufficiently with space velocity to explain this variation in yield of synthetic lubricating oil.

It is apparent from the data presented in Tables 30–34 that the tail gas from recycle operation with water gas has too high a concentration of carbon monoxide for use in a second-stage operation with cobalt catalysts. As mentioned in connection with Lurgi's development work, an iron catalyst having a use ratio H_2:CO of about 0.7 could be satisfactorily employed for the second stage following recycle operation on a cobalt catalyst. Ruhrchemie, however, planned in 1943 to add "con-

TABLE 34. RUHRCHEMIE RECYCLE OPERATION AT 7 ATM IN REACTOR NO. 10; AVERAGES FOR 6 MONTHS' OPERATION AT DIFFERENT SPACE VELOCITIES OF FRESH GAS

Charge number	11	10	22
Space velocity per hr of water gas	80	100	119
Operating temperature range, °C	190–214	191–220	203–225
Recycle ratio	3.0	3.0	3.0
Per cent conversion of $CO + H_2$	70.7	63.0	63.0
CH_4, per cent of CO converted	5.4	.....	9.5
CO_2, per cent of CO converted	2.2	.....	2.0
C_5+, g per cu m of $CO + H_2$	121.8	100.0	90.2
$C_3 + C_4$, g per cu m of $CO + H_2$	9.9	12.0	16.2
Space-time conversion, cu m of $CO + H_2$ per cu m catalyst per hr [a]	49.7	55.4	66.0
Weight per cent of C_5+ boiling in the range			
To 200°C	49.7	53.0	55.8
200°–320°C	25.7	25.0	24.5
320°–460°C	17.0	16.0	15.0
Above 460°	7.6	6.0	4.7
Olefins + oxygen compounds, volume per cent in			
Gasoline (to 200°C)	63	61	60
Diesel oil (200°–320°C)	45	43	41
Synthetic lubricating oil			
Weight per cent of 60°–200°C	48	42	36.4
Weight per cent of C_3+	19.1	17.4	14.8
Viscosity, 50°C	17	14	9.7
Viscosity, pole height	1.67	1.71	1.78

[a] The water gas used contained 12 per cent inerts.

verted" (water-gas shift reaction) gas rich in hydrogen to the recycle tail gas and to use cobalt catalyst in a second and a third stage operating at atmospheric pressure without recycle. In a memorandum [61] dated October 16, 1943, such a procedure is outlined. Because the durability of iron catalysts at atmospheric pressure is very poor and because Ruhrchemie had a considerable number of atmospheric-pressure reactors, it was desirable to employ cobalt catalysts in the second and third stages despite the additional cost of the "converted" gas necessary. It is difficult to understand, however, why Ruhrchemie did not plan to change to iron catalysts for the first-stage recycle operation. Possibly, the explanation is that commercial-scale operation with iron catalysts was not started until 1944. Use of iron catalysts in the first stage would have resulted in a higher concentration of hydrogen in the end gas, and,

[61] T.O.M. Reel 45, Bag 3,446, Item 17.

therefore, less converted gas would be needed to provide an adequate hydrogen concentration for the second stage with cobalt catalyst.

A detailed analysis of the liquid product from Ruhrchemie recycle operation with water gas on cobalt catalysts was made [62] in 1943 by the I.G. Farben. in its Leuna laboratories to determine its value as raw material for the oxo synthesis (addition of CO and H_2 to olefins to produce alcohols). Table 35 gives the alcohol, aldehyde, acid, ester, and olefin contents of seven fractions of the product. As the boiling point increases, the olefin content drops from 43 per cent in the C_6–C_7 fraction to 14.5 per cent in the C_{17}–C_{19} fraction. The olefin content was calculated from the iodine number and molecular weight of the fraction. In previous tables (particularly Tables 31–34) the value reported as "olefins plus oxygen compounds" was determined by measuring the solubility of the oil in a sulfuric-phosphoric acid mixture. For comparison purposes, this value is included in Table 35 as "SPL," and the difference

Table 35. Analyses of Liquid Product of Ruhrchemie Recycle Operation with Water Gas on Cobalt Catalyst

(All per cent figures except "SPL" are in weight per cent.)

Atmospheric-pressure boiling range, °C	To 105	105–175	175–218	218–255	255–290	290–320	320–360
Per cent of total	4.3	20.4	22.6	12.6	14.0	9.6	6.1
Density at 20°C	0.693	0.733	0.751	0.763	0.774	0.783	0.784
Olefins							
C number	6, 7	8, 9, 10	11, 12	13, 14	15, 16	17, 18	19, 20, 21
Per cent of fraction	43.0	41.9	41.0	33.3	28.0	19.9	14.5
Alcohols							
C number	3, 4	5, 6, 7	8, 9	10, 11	12, 13	14, 15	16, 17, 18
Per cent of fraction	12.2	13.0	9.3	9.0	8.4	7.1	4.8
Aldehydes							
C number	5	6, 7, 8	9, 10	11, 12	13, 14	15, 16	17, 18, 19
Per cent of fraction	4	1.0	0.0	0.0	0.0	0.0	0.0
Acids							
C number	1	2, 3, 4	5, 6, 7	7, 8, 9	10, 11	12, 13, 14	14, 15, 16, 17
Per cent of fraction	0.06	0.07	0.04	0.05	0.1	0.1	0.2
Esters							
C number	3, 4, 5	6, 7, 8, 9	9, 10, 11	11, 12, 13	13, 14, 15	15, 16, 17	17, 18, 19, 20
Per cent of fraction	0.0	0.9	0.6	0.7	0.8	3.4	4.6
SPL, volume per cent	65	62	51	43	38	32	....
SPL − (oxygen compounds + olefins)	6	5	0	0	0.7	1.5	....

between it and the sum of the olefins plus oxygen compounds shows that a very appreciable error occurs in the figures for the low-boiling fractions. As the "SPL" figures are in volume per cent, whereas the other data of Table 35 are in weight per cent, a part of the discrepancies is due

[62] T.O.M. Reel 134, Section VII, Item 5.

to differences in specific gravity of the oxygenated compounds and the hydrocarbons. The "SPL" determination is a fairly accurate measure of the olefins plus oxygen compounds for fractions boiling above 175°C.

The alcohol content, which is about 12–13 per cent in the low-boiling fractions, decreases to about 5 per cent in the high-boiling fractions. Aldehydes and acids are either absent or present in negligible amounts. Esters, which are present in very small amounts in the low-boiling fractions, increase to about 4 per cent in the high-boiling fractions. The fraction boiling below room temperature (0.5 per cent) and that boiling above 360°C (9.8 per cent) were not analyzed.

Gas-Recycle Operation with Beds of Iron Catalyst Granules Cooled by Indirect Heat Exchange

Recycle ratio of 3. Because of the exceedingly poor durability of iron catalysts in the synthesis at atmospheric pressure, virtually all the process development using iron catalysts was done at 10–20 atm pressure. The limited supply of cobalt in Germany during World War II resulted in an intensive development of iron catalysts which could replace cobalt, using the Ruhrchemie medium-pressure reactors. This development was described in Chapter 3, pp 305–309. The use ratio H_2:CO of iron catalysts without recycle of end gas usually is in the range 0.7–0.9. Because the H_2:CO ratio in the cheapest synthesis gas prepared by complete gasification of coal is 0.7–1.3, it is desirable to operate in this range. The use ratio of H_2:CO for any given iron catalyst can be materially increased by recycling 2 or 3 volumes of end gas per volume of fresh gas. The effect of recycle of end gas on the use ratio H_2:CO, on the yield, and on the product distribution is indicated by the data [63] of Table 36. The catalyst used in the pilot-plant tests of Table 36 was prepared from Luxmasse (residues from extraction of alumina from bauxite) by impregnation with copper nitrate solution, drying, reducing with hydrogen and screening to size. Commercial water gas was freed from sulfur and used as fresh feed gas. The tests were conducted at 20 atm pressure. Sampling for end-gas analysis of Table 36 appears to have been done before the charcoal scrubbers, as the recycle-gas analysis calculated from that of the fresh gas and end gas shows some discrepancies.

The data of Table 36 show an increase of H_2:CO use ratio from 0.89 when no recycling was done to 1.15 when 3 volumes of end gas per volume of fresh gas was recycled. The yield of C_3+ per cu m of inert-free fresh gas was 91 g with no recycle and 96–116 g with a recycle of 3 volumes of end gas per volume of fresh gas. The olefin plus oxygen com-

[63] T.O.M. Reel 36, Bag 3,451, Item 9; Bag 3,454, Item 17.

TABLE 36. RUHRCHEMIE PILOT-PLANT OPERATIONS IN SEPTEMBER 1940 AT 20 ATM PRESSURE, SHOWING EFFECT OF RECYCLE OF END GAS THROUGH A BED OF 100Fe:5Cu:10 KIESELGUHR CATALYST GRANULES

Test number	1			2			3			4			5			6		
Time of test, hr	152–296			296–488			612–756			827–970			987–1083			1083–1173		
Temperature, °C	250			250–252			253			253			253			253		
Recycle ratio	1.5			1.4			2.9			2.8			0.0			2.9		
Gas analysis, volume per cent	Fresh	End	Recycle	Fresh	End	Recycle	Fresh	End	Recycle	Fresh	End	Recycle	Fresh	End	Recycle	Fresh	End	Recycle
CO	6.3	36.2	17.2	6.7	33.2	17.0	6.8	33.0	27.5	6.4	30.4	25.8	7.1	33.5	....	6.6	32.5	25.8
C_nH_m	0.0	0.5	0.2	0.0	0.6	0.3	0.0	0.6	0.5	0.0	0.5	0.4	0.0	0.6	....	0.0	0.5	0.4
CO	38.6	12.4	28.8	38.2	14.5	28.7	38.0	17.2	21.7	38.7	19.0	23.0	37.3	11.1	....	38.4	18.8	23.7
H_2	49.6	35.8	44.6	49.4	36.6	43.9	48.6	30.5	34.8	48.3	29.8	35.0	49.4	39.1	....	49.2	31.0	35.0
CH_4	0.3	4.8	2.2	0.3	4.7	2.2	0.3	6.3	5.0	0.3	7.1	4.2	0.3	5.6	....	0.3	6.8	5.5
N_2	5.1	10.2	6.9	5.3	10.3	7.6	6.2	12.3	10.4	6.3	13.2	11.5	5.8	10.0	....	5.4	10.3	9.6
n		1.24	1.12	....	1.27	1.14	....	1.26	1.24	....	1.16	1.04	....	1.14	....	....	1.17	1.16
Contraction, per cent		50.5			47.5			51.4			51.9			44.6			47.3	
Conversion of	CO	H_2	$CO+H_2$	CO	H_2	$CO+H_2$	CO	H_2	$CO+H_2$	CO	H_2	$CO+H_2$	CO	H_2	$CO+H_2$	CO	H_2	$CO+H_2$
Per cent	84.2	64.3	73.0	80.1	61.2	69.4	77.9	69.6	73.2	75.6	70.2	73.1	83.4	56.3	67.9	74.2	66.9	70.2
Liquefaction, per cent	45.3	34.5	39.2	42.2	30.4	35.5	42.1	31.5	36.1	43.9	27.7	34.9	41.3	25.7	32.5	34.6	35.4	35.0
Conversion of $CO + H_2$ to	CH_4	CO_2	H_2O	CH_4	CO_2	H_2O	CH_4	CO_2	H_2O	CH_4	CO_2	H_2O	CH_4	CO_2	H_2O	CH_4	CO_2	H_2O
Per cent	13.8	18.9	14.5	16.1	17.6	15.1	18.5	14.5	17.7	18.6	12.9	20.7	19.0	19.5	13.7	20.4	17.1	12.2
Use ratio, H_2:CO		0.98			0.99			1.14			1.15			0.89			1.15	
Yield of	C_3+C_4	C_5+	H_2O	C_3+C_4	C_5+	H_2O	C_3+C_4	C_5+	H_2O	C_3+C_4	C_5+	H_2O	C_3+C_4	C_5+	H_2O	C_3+C_4	C_5+	H_2O
g per cu m of inert-free fresh gas	6.2	104	70	5.5	87	60	6.8	98	88	23	73	97	21	70	31	24	92	90
Boiling range, °C	To 200	200–320	Above 320	To 200	200–320	Above 320	To 200	200–320	Above 320	To 200	200–320	Above 320	To 200	200–320′	Above 320	To 200	200–320	Above 320
Weight per cent of C_5+	40.9	22.8	33.0	42.0	22.2	35.1	43.6	21.4	31.8	51.8	22.8	20.6	57.8	19.6	18.4	48.7	23.2	24.1
Olefin + oxygen compounds, volume per cent	49.9	30.9	....	45.5	38.0	....	61.2	46.6	....	62.7	46.0	.....	52.0	30.0	....	60.3	46.8	.....

pounds content of the gasoline and Diesel fraction was 10–20 per cent higher with a recycle ratio of 3 than when no recycle was employed. Methane production increased with increasing time of operation and showed no trend with recycle ratio.

Hall and Craxford [50] describe in more detail the preparation and induction of a Luxmasse catalyst by Ruhrchemie in 1940. The details of preparation and induction are given in Chapter 3, p 267, of this book.

Although the use ratio H_2:CO for most iron catalysts is in the range 0.7–0.9, a much higher ratio was achieved in laboratory experiments by Roelen at Ruhrchemie in 1944.[64, 65] In each of these tests 5 l of catalyst granules was tested in a double-tube reactor. Purified water gas at 10 atm pressure was used as fresh feed. Tests were made with and without recycle of end gas, and a study was made of the effect of type and amount of alkali in the catalyst and of the type of pretreatment, *ie*, whether reduced with hydrogen or inducted with synthesis gas. The catalysts used were precipitated with sodium carbonate from solutions of iron, calcium, and copper nitrates onto kieselguhr, and subsequently impregnated with potassium carbonate, hydroxide, or silicate. The bulk density of the catalysts was about 0.5.

It is apparent from Table 37 that pretreatment with water gas for 24 hr at 250°C and at atmospheric pressure results in an appreciably higher use ratio of H_2:CO (compare experiment 726 with 736, and experiment 738 with 735). Comparison of experiment 709 with 726 indicates that potassium silicate is a more desirable promoter than potassium carbonate as far as a higher H_2:CO use ratio and lower methane production are concerned. The product distribution from the catalysts of Table 37 shows no significant variation with either form of the potassium promoter or type of pretreatment. The appreciably higher yield of C_5+ per cubic meter of water gas in experiments 738 and 735 may be due either to the recycling of end gas or to the use of potassium hydroxide rather than the silicate or carbonate as promoter.

More details concerning the preparation of the type of catalyst used in the experiments of Table 37 are available.[50, 65, 66] A solution containing iron, calcium, and copper nitrates and water in the ratio (by weight) of 100Fe:5Cu:10CaO:2,000H_2O was heated to 98°C and run into a boiling soda solution containing 9–10 parts (by weight) of Na_2CO_3 per 100 parts of water. The amounts of solution were such that after the precipitation the *p*H was 6.8–7.0. For every 100 parts of iron, 30 parts of kieselguhr were stirred into the mixture, which then was filtered and washed

[64] T.O.M. Reel 34, Bag 3,440, Item 31.
[65] T.O.M. Reel 42, Bag 3,439, Item 22.
[66] T.O.M. Reel 37, Bag 3,451, Item 24.

TABLE 37. ROELEN'S TESTS ON 100Fe:5Cu:8CaO:30 KIESELHUGR:nK$_2$O CATALYSTS AT 10 ATM PRESSURE OF WATER GAS, FRESH-GAS SPACE VELOCITY 100 PER HR, IN 5-L DOUBLE-TUBE REACTOR, AT RUHRCHEMIE IN 1944

Test No., catalyst No.	709, PN31		726, PN43		738, PN47		730, PN43		735, PN47		736, PN43	
Potassium, form of	K_2CO_3		K_2SiO_3		KOH		K_2SiO_3		KOH		K_2SiO_3	
K, weight per cent of Fe	1.5		1.2		1.8		0.45		1.8		1.2	
Pretreatment	$3H_2 + 1N_2$, 1 hr, 300°C [a]						$1.3H_2 + 1CO$, 24 hr, 250°C [b]					
Recycle ratio [c]	0		0		3.0		0		3.0		0.0	
Time, hr	50	1,113	59	251	100	310	102	727	120	743	36	717
Temperature, °C	210	220	203	214	213	213.5	209	222.5	214	221.5	201	220
Use ratio, H_2:CO	0.8	0.76	1.03	0.90	0.98	0.98	1.32	1.08	1.35	1.15	1.21	1.11
CH_4, per cent of CO reacted	9.6	19.2	6.0	22.2	15.7	17.1	10.7	21.6	7.5	14.6	4.1	15.0
Contraction, per cent	48.3	63.8	38.0	56.0	66.9	68.8	47.2	51.4	61.9	70.0	44.9	55.0
C_5+, g per cu m [d]	79	95	65	79	103	105	76	73	103	107	77	85
C_5+ analysis												
Sampling time, hr	419	1,113	251		310		407	727	503 [e]	743 [e]	180	717
Weight per cent boiling in range												
To 200°C	71.3	61.5	67.8		57.0		62.5	56.4	41.8	44.7	63.0	58.4
200°–290°C	7.7	10.8	18.2		18.4		8.2	13.5	13.4	13.9	19.2	9.2
290°–320°C	5.8	4.5	5.8		5.0		6.6	5.2	5.8	4.5	9.6	7.3
320°–460°C	9.7	15.5	7.6		13.4		15.0	16.1	19.0	18.4	6.9	22.7
Above 460°C	4.8	6.2	0.6		5.3		6.7	7.5	18.6	17.7	1.3	1.5
Volume per cent of olefins plus oxygen compounds in fraction boiling in range												
To 200°C	52.5	51.0	60.0		60.5		55.0	57.0	65.0	54.0	58.0	61.0
200°–290°C	47.5	33.0	37.5		48.0		37.5	40.5	56.5	45.0	41.0	35.0
290°–320°C	43.0	27.0	24.5		37.0		19.0	24.0	43.0	38.5	34.4	30.0

[a] Atmospheric-pressure reduction, 300 l of $3H_2 + 1N_2$ per hr.
[b] Atmospheric-pressure induction, 500 l of $1.3H_2 + 1CO$ per hr.
[c] Volumes of end gas per volume of fresh feed.
[d] Grams of C_5+ per cubic meter of water gas of composition:

CO_2	CO	H_2	CH_4	N_2
7.0	38.0	49.1	0.2	5.7

[e] Gasol, $C_3 + C_4$, yield was 8.0 and 15.9 g per cu m of water gas at 503 and 743 hr, respectively, in test 735.

with hot distilled water until the sodium nitrate content of the finished catalyst was about 0.5–0.7 part per 100 parts of iron. Usually 200–220 parts of wash water per part of iron were adequate; an excess should be avoided so as not to decrease the calcium oxide content of the precipitate. After washing, the wet filter cake was impregnated with the desired amount of KOH, K_2CO_3, or K_2SiO_3 by repulping it in a kneading machine with a measured amount of dilute solution of the potassium salt and again filtering. A concentration of about 100 g per l of KOH, K_2CO_3, or K_2SiO_3 was used. The filter cake was dried at 110°C, crushed, and screened to 2–3-mm particles.

In 1941–1943 Ruhrchemie operated several large pilot plants with catalyst volumes ranging from 0.1 to 4.5 cu m, at 10–20 atm pressure, using an iron catalyst the composition of which was 100Fe:5Cu:(8–10)CaO:150 kieselguhr and $1.3H_2:1CO$ fresh gas feed with a recycle of 3 volumes of end gas per volume of fresh feed. The preparation of the catalyst was similar to that described above for the iron catalysts used in obtaining the data of Table 37, except that K_2CO_3 rather than Na_2CO_3 was used for precipitation and the precipitate was not impregnated with potassium hydroxide. This catalyst was reduced with hydrogen at 300°C. It was not as active as those prepared by Roelen in 1943–1944, the operating temperature range being 230°–265°C. These tests [60, 67–70] were of 2,000–5,000 hours' duration. The activity of the catalyst, as measured by the space-time-yield of C_3+, decreased gradually during operation, but the product distribution changed more rapidly from an initial 50–60 per cent to 20–30 per cent boiling above 320°C after 2 or 3 months. Most of these pilot-plant operations were directed towards specification of a plant for the Societa Italiana Carburanti at Arrezo in Italy. The specifications for this project,[71] written in 1942–1943, may be used to summarize the results of the 1941–1943 pilot-plant iron catalyst operations.

Water gas from gasification of brown coal was compressed to 25 atm and washed with water to remove CO_2 and some of the H_2S. Its composition after washing was as follows:

Constituent	CO_2	CO	H_2	CH_4	N_2
Volume per cent	3–5	39–41	50–52	2.5	2.5–3.5
Constituent	H_2S		Organic sulfur		
g per 100 cu m	Up to 20		Up to 4		

[67] T.O.M. Reel 35, Bag 3,452, Item 1.
[68] T.O.M. Reel 39, Bag 3,450, Items 42 and 43.
[69] T.O.M. Reel 45, Bag 3,446, Item 12.
[70] T.O.M. Reel 47, Bag 3,446, Items 72, 73, 74, 77, 78, and 79.
[71] T.O.M. Reel 39, Bag 3,450, Item 46.

This gas was then passed at 21 atm and 280°C over alkalized iron oxide for sulfur removal. The purified gas contained less than 0.2 g of sulfur per 100 cu m. The synthesis was conducted at 20 atm and 235°–265°C in the standard double-tube medium-pressure reactors. The specified operation was in two stages with recycling in the first stage of 2.5 volumes of end gas per volume of fresh gas. Gas compositions and contractions were as follows (in volume per cent):

	Synthesis Gas	End Gas, First Stage	End Gas, Second Stage	
CO_2	4.5	23.8	41.0	
CO	39.0	25.0	12.4	
H_2	50.0	32.0	15.9	
CH_4	3.5	12.8	21.2	
N_2	3.0	6.4	9.5	
Contraction		52.3	32.5	
Total contraction				68.5

The total yield of C_3+ was 140 g per cu m of $CO + H_2$ charged; of this 14 g was $C_3 + C_4$. The CH_4 production was 23 g per cu m of $CO + H_2$. The product distribution in weight per cent was:

Gasol	Liquid Product Boiling in the Range, °C		
$C_3 + C_4$	35°–200°	200°–320°	Above 320°
10	31	20	39

The olefin content of the gasol was 60 volume per cent. The olefins plus oxygen compounds constituted 65–70 per cent of the gasoline fraction and 50–55 per cent of the Diesel oil fraction. The figures for product distribution are averages for the 3 months' life of the catalyst. After 80–90 days' operation, the catalyst was extracted with a gasoline fraction (170°–200°C) to recover its wax content before discharging the catalyst from the reactor.

A pilot-plant operation, using a low-temperature iron catalyst of the type used to obtain the data of Table 37 and a commercial-size double-tube medium-pressure reactor, was made by Ruhrchemie [60] in February to August 1944. The data for this operation are given in Table 38. The performance recorded in this table is remarkable in many ways. At a virtually constant operating temperature, 215°–218.6°C, for 3,550 hr there was no significant change in contraction and product distribution; there were only about a 10 per cent drop in yield of C_3+ and a 10 per cent increase in CH_4 production. The olefin content of the oil and the quality of the lubricating oil synthesized from the 60°–200°C fraction of the product increased appreciably during the 3,550 hr of the operation. The space-time-yield of C_3+ dropped about 25 per cent, indicating a

TABLE 38. RUHRCHEMIE PILOT-PLANT OPERATION, USING A LOW-TEMPERATURE IRON CATALYST; 10 ATM PRESSURE, COMMERCIAL-SIZE, DOUBLE-TUBE MEDIUM-PRESSURE REACTOR (NO. 11, CHARGE 14.)

Date	Feb. 1944			Mar.–Apr. 1944			Apr.–May 1944			May–June 1944			June–Aug. 1944		
Time, hr	0–724			724–1,471			1,471–2,249			2,249–2,923			2,923–3,550		
Temperature, °C	218.6			218.6			215.1			216.8			218.6		
Space velocity per hr of fresh gas	95			100			87			84			80		
Recycle ratio	2.95			3.02			3.00			2.90			2.95		
Gas analyses, volume per cent	Fresh	End	Recycle	Fresh	End	Recycle	Fresh	End	Recycle	Fresh	End	Recycle	Fresh	End	Recycle
CO_2	6.4	30.2	24.2	6.5	30.1	24.2	7.1	29.4	23.8	6.5	27.9	22.4	6.5	27.7	22.3
C_nH_m	....	0.3	0.2	....	0.2	0.1	....	0.2	0.2	....	0.0	0.23	....	0.3	0.22
CO	38.9	18.4	23.5	38.7	18.4	23.4	37.8	18.7	23.5	38.4	20.1	24.8	38.1	20.1	24.6
H_2	49.4	39.6	41.6	49.4	38.7	41.4	50.0	40.0	42.4	50.0	40.0	42.6	49.5	39.3	41.8
CH_4	0.3	2.7	2.1	0.3	2.8	2.2	0.3	2.8	2.2	0.3	2.8	2.2	0.3	2.8	2.2
N_2	4.9	9.4	8.3	5.0	9.7	8.6	4.7	8.8	7.8	4.7	8.8	7.8	5.5	9.8	8.7
n	....	1.04	....	....	1.00	....	....	1.00	....	....	1.02	.....	....	1.01	.....
Contraction, per cent	46.2			48.1			44.4			46.1			45.1		
Use ratio, H_2:CO	0.98			1.01			1.01			1.03			1.03		
Conversion of	CO	H_2	$CO+H_2$	CO	H_2	$CO+H_2$	CO	H_2	$CO+H_2$	CO	H_2	$CO+H_2$	CO	H_2	$CO+H_2$
Per cent	74.3	57.7	66.0	75.4	59.4	67.4	72.6	55.6	64.1	72.0	57.2	46.1	71 2	56.3	63.8
Conversion of CO to	CH_4		CO_2	CH_4		CO_2	CH_4		CO_2	CH_4		CO_2	CH_4		CO_2
Per cent	4.0		33.9	4.0		31.4	4.6		33.6	4.3		31.0	4.5		32.3
Yield of	C_3+C_4		C_5+	C_3+C_4		C_5+	C_3+C_4		C_5+	C_3+C_4		C_5+	C_3+C_4		C_5+
g per cu m of inert-free fresh gas	10.9		106	12.6		92	12		90	13		88	15		89
C_3+, kg per cu m of catalyst per hr	11.1			10.5			8.9			8.5			8.3		
Boiling range, °C	To 200		200–320	To 200		200–320	To 200		200–320	To 200		200–320	To 200		200–320
Weight per cent of C_5+	31.7		15.2	29.6		16.2	30.5		15.1	29.7		17.8	31.8		15.3
Boiling range, °C	320–460		Above 460	320–460		Above 460	320–460		Above 460	320–460		Above 460	320–460		Above 460
Weight per cent of C_5+	16.5		36.6	17.8		36.4	18.3		37.2	16.5		35.6	19.9		33.0
Olefins + oxygen compounds, volume per cent															
Boiling range, °C	To 200		200–320	To 200		200–320	To 200		200–320	To 200		200–320	To 200		200–320
Volume per cent	68		43	69		49	71		53	72		54	72		55
Synthetic lubricating oil															
Weight per cent of 60°–200°C fraction	43.6			44.9			48.4			51.1			52.3		
Viscosity, 50°C	10.1			12.1			11.9			11.4			12.9		
Viscosity, pole height	1.74			1.65			1.65			1.61			1.69		

decrease in catalyst activity. The H_2:CO use ratio was in the range 0.98–1.03. It is probable on the basis of Roelen's experiments described in Table 37 that an average use ratio of 1.3 could have been obtained by replacing the reduction with hydrogen by a treatment with water gas at atmospheric pressure and at 250°C for 24 hr. The use of a second stage then would have made possible a yield of the order of 150–160 g of C_3+ per cu m of CO + H_2.

Effect of recycle ratios above 3 with granular beds of iron catalyst; the "synol process." The effect of recycle of end gas through beds of granules of iron catalysts was studied at Rheinpreussen [72] in 1943–1944. The data of Table 39 were obtained from laboratory tests

Table 39. Effect of Recycle Ratio Laboratory Tests at 10 atm of Water Gas with Fe-Cu-Dolomite-K_2CO_3 Catalyst; Space Velocity per hr, 95

Time, hr	Temperature, °C	Recycle Ratio, End Gas to Fresh Gas	H_2:CO Ratio in Fresh Gas	H_2:CO, Use Ratio	Grams per Cubic Meter of Inert-Free Water Gas					Per Cent CO Reacted
					Calculated Yield		Measured Yield			
					CH_4	C_1+	C_1+	Gasol	CH_4	
40	225	5.5	1.3	1.26	11	163	...	....	....	82
61	226	6	1.3	1.23	18	178	...	....	....	89
70	225	7	1.37	1.23	17	180	...	....	....	91
79	227	9	1.37	1.33	17	183	179	16.7	22.5	92
232–341	225	8.2	1.36	1.32	25	169	...	....	....	87
405–418	225	4.6	1.38	1.29	26	165	162	14.0	24.5	85
492–543	222	3	1.3	1.17	25	150	...	....	....	84
562	217	0	1.33	0.94	21	129	...	....	....	86
609–676	226	3	1.46	1.26	26	164	...	....	....	90
808	227	4	1.46	1.29	27	165	...	....	....	86

in which 170 cc of catalyst, weighing 105 g and containing 40 g of Fe, was contained in a bed 80 cm in depth. No details are given concerning the construction of the reactor and its cooling system. The composition of the catalyst was in the range 100Fe:(1–10)Cu:(50–100)dolomite:(0.1–3.0)K_2CO_3. The method of preparation is outlined in Chapter 3, p 268. The catalyst was pretreated for several hours with pure CO at 0.1–0.2 atm and at 300°C. Water gas at 10 atm of about the following analysis, in volume per cent, was used in the synthesis operation:

CO_2	CO	H_2	CH_4	N_2
8.2	36.4	46.4	0.5	8.5

[72] F.I.A.T. Reel X-116, Frames 1,684–765.

The yield of methane and of total hydrocarbons (C_1+) given in columns 6 and 7 of Table 39 was calculated from gas analyses. The C_1+ yield, directly measured at the 79 and 405–418 hr intervals, is given in columns 8, 9, and 10 of Table 39. The use ratios for recycle ratios of 0, 3, 5, and 9 are about 1, 1.2, 1.25, and 1.33, respectively. Comparison of the C_1+ yield (column 7, Table 39) for the 492–543, 562, and 609–676 hr intervals shows a marked increase in going from no recycle of end gas to a recycle ratio of 3. A smaller increase in the C_1+ yield is apparent also for recycle ratios of 6–9 as compared with the yield at a recycle ratio of 3. The methane yield shows no significant change with varying recycle ratio but appears to increase with increasing catalyst age. Similar results are given [72] for the catalyst 100Fe:10Cu:20MgO:50 kieselguhr:$1K_2CO_3$ whose preparation is described in a F.I.A.T. reel.[73]

At a recycle ratio in the range 2.5–2.8 the Rheinpreussen experimenters found [67] that a higher H_2:CO use ratio and lower methane yield were obtained when operating at 40–50 per cent conversion of CO as compared

Table 40. Effect of Extent of CO Conversion on Use Ratio and Methane Production; Laboratory Tests at 10 atm of Water Gas with Fe-Cu-MgO-Kieselguhr-K_2CO_3 Catalyst

Time, hr	Temperature, °C	H_2:CO in Fresh Gas	H_2:CO, Use Ratio	Hourly Space Velocity	Per Cent CO Reacted	Grams per Cubic Meter of Inert-Free Water Gas		C_1, per cent of C_1+
						C_1+	C_1	
18	215	1.26	0.90	101	91.4	152	12	7.9
38	216	1.26	0.93	101	90.0	158	7	4.4
63	215	1.26	0.93	92	90.0	157	13	8.3
108	217.5	1.27	0.90	93	89.5	155	14	9.0
208	219.5	1.27	0.89	91	93.6	162	24	14.8
255	219.5	1.28	0.90	88	91.5	154	19	12.3
351	221	1.32	0.99	84	80.3	140	16	11.4
394	223	1.30	0.93	78	82.0	132	15.5	11.7
450	223	1.26	0.97	84	73.0	127	10.3	8.1
495	222.5	1.23	0.77	40	95.6	145	17.6	12.1
511	226.5	1.26	1.05	300	42.0	79	3.6	5.8
566	226	1.27	1.18	320	37.0	64	5.8	9.1
615	225	1.28	1.13	270	40.0	72	5.7	7.9
662	225	1.24	1.11	340	52.0	96	2.6	2.7

[73] F.I.A.T. Reel X-116, Frames 1,670–2.

with operation at 85–90 per cent. The methane production varied also with age of the catalyst. The data supporting these conclusions are shown in Table 40. The kieselguhr-containing catalyst [73] was used in these tests.

The type of pretreatment of the dolomite-containing catalyst [72] had a marked effect on the methane production and durability of the catalyst in the synthesis. Thus, when pretreated at atmospheric pressure with $2H_2 + 1CO$ gas (containing 7–9 per cent CO_2 and about an equal amount of N_2) at 2,000–3,000 hourly space velocity and 300°–320°C for 6 hr, this catalyst produced only about one-half as much methane as when pretreated with pure CO at 0.1 atm at 300°–320°C. After the $2H_2 + 1CO$ pretreatment, the catalyst was operated for over 2,000 hr without appreciable deterioration, whereas after the pure CO pretreatment not more than about 1,000 hr of satisfactory performance was possible. The data for these tests are given in Table 41. The comparison attempted in this table is difficult because 2.5 volumes of end gas to 1 volume of fresh gas were recycled in the case of the pure-CO-pretreated catalyst, whereas there was no end-gas recycle in the synthesis after the $2H_2 + 1CO$-pretreated catalyst. The results of Table 39, however, indicate little change in grams of CH_4 per cubic meter of inert-free water gas with recycle ratio. The use ratio H_2:CO for the $2H_2 + 1CO$-pretreated catalyst of Table 41 probably would have been about 1.2 if 2–3 volumes of end gas per volume of fresh gas had been recycled. Less CO_2 and more oil would have been produced.

A catalyst in which calcium carbonate was substituted for the dolomite and which contained in parts by weight $100Fe:90CaCO_3:1K_2CO_3$ also was tested [72] after pretreatment with $2H_2 + 1CO$ at 1 atm and at 300°–320°C. Synthesis was conducted with 10 atm of water gas (about $1.3H_2 + 1CO$) at 220°–250°C, with an hourly space velocity of about 100 and with no end-gas recycle. This catalyst produced only traces of methane, but its useful life was only 200–300 hr, after which the activity decreased rapidly.

The I.G. Farben. catalyst used in the Schwarzheide tests (Chapter 3, p 305) was a synthetic-ammonia catalyst consisting of 97 per cent fused magnetite Fe_3O_4 plus 2.5 per cent alumina, and about 0.5 per cent K_2O. This catalyst, after virtually complete reduction with dry hydrogen at 450°–500°C, is quite active at 190°–220°C. In 1941–1942, the I.G. Farben. found that operation in this temperature range, at 20 atm pressure, in four stages, with removal of carbon dioxide between stages, yields a liquid product containing 40–60 per cent of alcohols.[74] Later (1943–1944) experiments showed that the alcohol content of the products

[74] T.O.M. Reel 134, Navy 5,811, *Repts.* 283 and 326.

TABLE 41. ACTIVITY OF Fe-Cu-DOLOMITE-K_2CO_3 CATALYST PRETREATED WITH 0.1 ATM OF PURE CO AT 300°–320°C, COMPARED WITH ACTIVITY OF THE SAME CATALYST PRETREATED AT THE SAME TEMPERATURE WITH 1 ATM OF $2H_2 + 1CO$; LABORATORY TESTS WITH 10 ATM OF WATER GAS (ABOUT $1.3H_2 + 1CO$)

Time, hr	Temperature, °C	Per Cent CO Reacted	H_2:CO, Use Ratio	Oil + Gasol, g per cu m of inert-free water gas	CH_4, per cent of oil + gasol
Synthesis with recycle ratio of 2.5, after pretreatment with pure CO, 0.1 atm, 300°–320°C, 100–500 SVH					
66	205	86	1.18	149	18
112	205	94.6	1.04	150	16
140	208	87	1.28	143	13.3
167	208	91	1.12	155	12.9
212	208	90.5	1.14	156	12.8
351	214	79	1.20	134	14.9
393	217	86.5	1.20	150	13.3
418	217	86	1.13	138	14.5
Synthesis with no end-gas recycle, after pretreatment with $2H_2 + 1CO$, 1 atm, 300°–320°C, 2,000–3,000 SVH					
100	209	78	0.98	140	3.8
200	216.5	81	0.92	138	3.8
400	219	79	0.94	135	2.8
600	220	88	0.84	143	7.0
800	220.5	84	0.90	137	6.5
1,000	220	90	0.89	143	7.0
1,200	220	91	0.88	148	5.2
1,400	220	90	0.85	145	3.8
1,600	220	90	0.92	151	2.3
1,800	220	91	0.89	149	5.6
2,000	220	89	0.89	146	4.5
2,153	220	89	0.87	144	5.4

could be increased appreciably by recycling about 10 volumes of end gas per volume of fresh gas and removing in each cycle the readily condensable products, including virtually all the water of reaction.[40, 75, 76] With a minimum of water vapor in the recycle gas, the formation of

[75] T.O.M. Reel 13, Bag 3,043, Item 3.
[76] T.O.M. Reel 86, Bag 3,979, Item 78.

carbon dioxide is reduced to the point where a small percentage of this constituent in the fresh gas is tolerable. Another advantage of recycling is an increase in the useful life of the catalyst; this is about 3 months without recycle and 7 months with recycle of 10 volumes of end gas per volume of fresh gas. At a total-feed space velocity of about 2,500 per hour, 90 per cent conversion of water gas (1:1–1:1.3 $CO:H_2$) containing 6 per cent of inerts was achieved in two stages: 70 per cent in the first and 20 per cent in the second stage. The space-time conversion in the synol

TABLE 42. ANALYSES OF SYNOL PRODUCTS BY DR. REISINGER AT LEUNA
(REACTOR 13/1, DEC. 20, 1940, TO JAN. 6, 1941.)

Fraction, °C	Weight Per Cent of C_3+	Alcohols					
		Weight Per Cent of Fraction	Weight Per Cent of C_3+ × 100	C No. Distribution, Weight Per Cent of C_3+ × 100			
C_3–C_4	8.4	0.0					
to 40	1.9	0.0	0		0	0	
40–60	6.5	3.5	22.7	C_1	22.7	41.7	C_1
			47.6	C_1	19.0		
60–80	5.6	8.5	290 [a]	C_2	28.6	54.6	C_2
			78.0	C_2	26.0	+290 [a]	
80–100	5.2	15.0	197 [a]	C_3	52.0	85.6	C_3
				C_3	34.5	+197 [a]	
100–120	5.0	23.0	115.0	C_4	80.5	125.0	C_4
				C_4	44.5		
120–140	4.5	33.0	148.5	C_5	104.0	170.9	C_5
				C_5	66.9		
140–160	4.2	45.5	191.1	C_6	124.2	175.7	C_6
				C_6	51.5		
160–180	4.3	54.0	232.1	C_7	180.6	229.8	C_7
				C_7	49.2		
180–200	3.9	60.0	234.0	C_8	184.8	213.2	C_8
				C_8	28.4		
200–220	4.1	63.0	258.3	C_9	229.9	229.9	C_9
220–240	3.6	65.5	235.9	C_{10}	235.9	260.2	C_{10}
				C_{10}	24.3		
240–260	3.6	67.5	243.0	C_{11}	218.7	218.7	C_{11}
260–280	3.2	68.0	217.6	C_{12}	217.6	217.6	C_{12}
				C_{13}	137.0	137.0	C_{13}
280–300	3.2	68.5	219.2	C_{14}	82.2	113.9	C_{14}
				C_{14}	31.7		
300–320	2.8	68.0	190.4	C_{15}	158.7	158.7	C_{15}
				C_{16}	126.0	126.0	C_{16}
320–340	2.8	67.5	189.0	C_{17}	63.0	63.0	C_{17}
				C_{18}	184.8	184.8	C_{18}
340–360	2.8	66.0	184.8	C_{20}	163.9	163.9	C_{20}
360–380	2.6	63.0	163.9	C_{22}	139.2	139.2	C_{22}
380–400	2.4	58.0	139.2				
400–420	2.2	50.5	111.1	$>C_{22}$	111.1	680.6	$>C_{22}$
420–440	2.0	41.5	83.0	$>C_{22}$	83.0		
>440	15.2	32.0	486.5	$>C_{22}$	486.5		

TABLE 42. ANALYSES OF SYNOL PRODUCTS BY DR. REISINGER AT LEUNA
(*Continued*)

(REACTOR 13/1, DEC. 20, 1940, TO JAN. 6, 1941.)

Fraction, °C	Olefins + Unsaturated Alcohols					Esters	
	Weight Per Cent of Fraction	Weight Per Cent of $C_3+ \times 100$	C No. Distribution, Weight Per Cent of $C_3+ \times 100$			Weight Per Cent of Fraction	Weight Per Cent of $C_3+ \times 100$
C_3–C_4 to 40	77.0	146.3	C_4 24.4	24.4	C_4	0.20	0.4
			C_5 121.9	367.9	C_5		
40–60	67.4	438.2	C_5 246.0			0.31	2.0
			C_6 192.2				
60–80	78.2	437.9	C_6 437.9	675.6	C_6	0.5	2.8
80–100	38.1	198.2	C_6 45.5			0.2	1.0
			C_7 152.7	264.7	C_7		
100–120	41.8	209.0	C_7 112.0			0.36	1.8
			C_8 97.0	268.0	C_8		
120–140	45.7	205.7	C_8 171.0			0.78	3.5
			C_9 34.7				
140–160	20.9	87.8	C_9 87.8	136.6	C_9	2.05	8.3
160–180	19.6	84.3	C_9 14.1			2.23	9.6
			C_{10} 70.2	87.0	C_{10}		
180–200	21.5	83.8	C_{10} 16.8			2.73	10.6
			C_{11} 67.0	92.5	C_{11}		
200–220	30.75	126.1	C_{11} 25.5			2.57	10.5
			C_{12} 100.6	119.7	C_{12}		
220–240	26.75	96.2	C_{12} 19.1			3.77	13.6
			C_{13} 77.1	91.5	C_{13}		
240–260	25.28	91.0	C_{13} 14.1			2.66	9.6
			C_{14} 76.6	83.5	C_{14}		
260–280	21.58	69.1	C_{14} 6.9			3.6	11.5
			C_{15} 62.2	62.2	C_{15}		
280–300	24.9	79.7	C_{16} 59.8	59.8	C_{16}	3.5	11.2
			C_{17} 19.9	52.4	C_{17}		
300–320	23.2	65.0	C_{17} 32.5			3.8	10.6
			C_{18} 32.5	48.6	C_{18}		
320–340	23.0	64.4	C_{18} 16.1			4.0	11.2
			C_{19} 48.3	48.3	C_{19}		
340–360	24.1	67.6	C_{20} 56.4	56.4	C_{20}	1.48	4.1
			C_{21} 11.2	33.7	C_{21}		
360–380	26.0	67.5	C_{21} 22.5			3.4	8.8
			C_{22} 22.5	22.5	C_{22}		
380–400	27.1	65.0	C_{23} 22.5	22.5	C_{23}		
400–420	39.6	87.1	C_{24} 65.0	65.0	C_{24}	2.44	5.9 [b]
420–440	35.0	70.0				4.0	8.8
>440	40.0	608.0	$>C_{24}$ 765.1	765.1	$>C_{24}$	1.95	3.9
						1.50	22.8

TABLE 42. ANALYSES OF SYNOL PRODUCTS BY DR. REISINGER AT LEUNA
(*Continued*)

(REACTOR 13/1, DEC. 20, 1940, TO JAN. 6, 1941.)

Fraction, °C	Ketones and Aldehydes		Acids		Paraffins		Apparent Excess above 100 Per Cent Because of Unsaturated Alcohols	
	Weight Per Cent of Fraction	Weight Per Cent of C_3+ × 100	Weight Per Cent of Fraction	Weight Per Cent of C_3+ × 100	Weight Per Cent of Fraction	Weight Per Cent of C_3+ × 100	Weight Per Cent of Fraction	Weight Per Cent of C_3+ × 100
C_3–C_4								
to 40	3.0	5.7	0.0	0.0	19.8	37.6		
40–60	3.5	22.7	0.0	0.0	25.9	164.4		
60–80	3.8	21.3	0.0	0.0	9.0	50.4		
80–100	7.4	38.5	0.0	0.0	39.3	204.3		
100–120	7.2	36.0	0.02	0.1	27.2	138.1		
120–140	8.2	36.9	0.02	0.1	12.3	55.3		
140–160	8.6	36.1	0.05	0.2	22.9	96.2		
160–180	7.3	31.4	0.04	0.2	16.83	72.4		
180–200	7.4	28.9	0.04	0.2	8.33	32.5		
200–220	7.5	30.7	0.68	2.8	Cannot be determined by known methods because of unsaturated alcohols		+4.5	18.4
220–240	7.8	28.1	0.18	0.6			+4.0	14.4
240–260	7.9	28.4	0.16	0.6			+3.5	12.6
260–280	8.7	27.8	0.12	0.4	....	...	+2.0	6.4
280–300	4.3	13.8	0.1	0.3	....	...	+1.3	4.2
300–320	3.3	9.2	0.11	0.3	1.59	4.5		
320–340	2.7	7.5	0.2	0.6	2.6	7.3		
340–360	0.8	2.2	0.36	1.0	7.26	20.3		
360–380	0.0	0.0	1.0	2.6	6.6	17.2		
380–400	0.0	0.0 [c]	2.9	7.0	9.56	22.9		
400–420	0.0	0.0	8.0	17.6	0.0	0.0	+2.1	4.6
420–440	0.0	0.0	18.4	36.8	3.15	6.3		
>440	0.0	0.0	24.3	369.3	2.2	33.4		

[a] From reaction water, calculated as per cent of oil product.
[b] Very uncertain from here to >440.
[c] Oxidation during distillation of $C_{22}+$.

process with a recycle ratio of 10 is about 150 cu m of CO + H_2 per hr per cu m of catalyst. The specific yield is 170 g of C_3+ per cu m of CO + H_2 reacted. About 10 per cent of the reacted gas is converted to methane. Of the 170 g of C_3+, 35 g is gasol, and 30 g boils above 400°C.

The alcohol, olefin, ester, acid, and saturated hydrocarbon contents of the synol product are given in Table 42 in weight per cent and in

Table 43 in mole per cent. Table 42 is a copy of Dr. Reisinger's analysis.[75] On the basis of data in other documents [75, 76] the product distribution in the synol process was estimated to be, in weight per cent: 9 methane, 3.5 ethane + ethylene, 17 gasol, 60.5 oil, 10 organic water-solubles. The water-solubles contain, in weight per cent, approximately 10 methanol, 30 ethanol, 40 propanol, and 10 butanol + higher alcohols. From these distribution estimates and the data of Table 42 to obtain the detailed carbon number distribution in the oil, the data of Table 43

TABLE 43. DISTRIBUTION OF SYNOL PRODUCT, MOLE PER CENT [a]

C Number	Alcohols	Olefins	Saturated Hydrocarbons	Total	C Number	Alcohols	Olefins	Saturated Hydrocarbons	Total
1	2.35	.....	37.3	39.65	13	0.269	0.120	0.032	0.421
2	4.36	5.98	1.37	11.71	14	0.209	0.131	0.020	0.360
3	4.55	9.68	2.33	16.56	15	0.275	0.090	0.019	0.384
4	1.47	7.41	1.79	10.67	16	0.203	0.108	0.009	0.320
5	0.765	2.09	0.67	3.525	17	0.096	0.084	0.008	0.188
6	0.681	3.17	0.78	4.631	18	0.141	0.078	0.011	0.230
7	0.783	1.075	0.87	2.728	19	0.140	0.072	0.007	0.219
8	0.645	0.938	0.39	1.973	20	0.123	0.078	0.007	0.208
9	0.627	0.424	0.36	1.411	21	0.110	0.045	0.006	0.161
10	0.651	0.245	0.19	1.086	22	0.191	0.030	0.006	0.227
11	0.502	0.125	0.13	0.757	23	0.848 [b]	0.028	0.006	.
12	0.460	0.203	0.045	0.708	24	. . .	0.078	0.039 [c]	.....
					>24	. . .	0.824	.	.....

[a] 7.2 weight per cent of esters + aldehydes + acids is not included in above distribution.
[b] >22 C number.
[c] >23 C number.

were calculated. It is probable that the yield of methanol in the reaction water is only a fraction of the actual yield. Because of its volatility a large fraction of the methanol probably was collected as gasol. No correction for this was made in calculating the mole percentages in Table 43. On a weight per cent basis (Table 42) it is apparent that the bulk of the C_3+ product consists of alcohols and olefins with minor amounts of saturated hydrocarbons, esters, ketones, aldehydes, and very small amounts of fatty acids. On a mole per cent basis (Table 43) the C_1 fraction is largely methane, whereas all other fractions contain only 10–20 per cent of saturated hydrocarbons. About 37 mole per cent of the product is methane. The C_2–C_{10} portion comprises 55 mole per cent of the total product, including methane, and about 87 mole per cent of the C_2+ product. Of the C_2+–C_{10} portion, 30 mole per cent is alcohol, 54 mole per cent is olefin, and 16 mole per cent is saturated hydrocarbon. The composition of the synol product is a challenge to the chemical in-

dustry to provide suitable processes for its utilization. This composition is also of significance in discussions of the mechanism of the Fischer-Tropsch synthesis.

Processes Using Fixed Beds of Granular or Pelleted Catalysts with Internal Cooling by Direct Heat Exchange

THE HOT-GAS RECYCLE

In 1938–1939 W. Michael of the I.G. Farben. developed the hot-gas-recycle process [75,77,78] in which the heat of reaction was removed as sensible heat in the reaction gas. The temperature rise in the catalyst bed from entrance to exit of the reaction gas was limited to about 10°C. This necessitated a very high rate of recycle of hot gas of the order of 100 volumes of end gas per volume of fresh gas, corresponding to a contact time of about 0.7 sec. The heat of reaction was absorbed in an external heat exchanger placed in the recycle circuit. Operating temperature was 320°–330°C and operating pressure 20 atm. The catalyst was prepared by making a paste of iron powder (obtained from decomposition of iron carbonyl) with a dilute solution of borax (1 per cent of borax based on iron). The paste was formed into 1-cm cubes; they were dried and heated in a hydrogen atmosphere at 850°C for several hours before use in the synthesis.

The conversion per cycle was about 1 per cent of the fresh gas. The latter was purified water gas with a hydrogen:carbon monoxide ratio of about 0.9. One per cent of fresh gas was added per cycle, and an equivalent amount of end gas was removed, passed through a condensation and product recovery system, and thence to a second stage which was about one-fourth the size of the first stage. All the available data on the process were obtained from a pilot plant operated for several months, using a single bed of catalyst, 87 cm deep and 78 cm in diameter. The gas flow was from top to bottom of the catalyst bed, and baffles were inserted at the gas inlet to avoid turbulence and obtain uniform flow through the reactor.

The motor casing of the gas recycle compressor was under 20 atm pressure, the fresh gas being charged into the motor casing to prevent leakage of recycle gas into the motor space. Gas temperature at the

[77] H. V. Atwell, A. R. Powell, and H. H. Storch, *Fischer-Tropsch T.A.C. Rept.* Sn Mc 1, PB 2,051 (1945).

[78] *The* CO + H_2 *Synthesis at I.G. Farben.*, vol. 1, Part C, prepared under direction of W. Faragher and J. Foucher at Ludwigshafen in 1947. Translation published as *F.I.A.T. Final Rept.* 1,267, PB 97,368.

inlet of the converter was 320°C, and at the outlet 330°C. The outlet gas was cooled to 323°C in a heat exchanger and then to 320°C by addition of cold fresh gas. The end gas removed from the recycle was passed at 20 atm through a hot (100°C) separator, water coolers at 20°–30°C, and finally a refrigerated separator at minus 40°–45°C. Ahead of the refrigerated separator, water vapor was removed by calcium chloride. After the refrigerated separator, carbon dioxide in the gas was removed by scrubbing with "alkazid" solution and the CO_2-free tail gas was sent to the second stage.

To start the plant, the heat exchanger between the recycle compressor and the reactor was heated by steam at 20 atm and gas recycling was started. The temperature was increased to 320°C by using an electric heating system in the gas recycle line. After a few hours, a steady state was reached so that only minor adjustments occasionally were necessary. The conversion was 78–82 per cent of the entering $CO + H_2$, and the CO_2 content of the tail gas 30–45 per cent. The space-time-yield was 0.8 kg product per l of catalyst space per 24 hr, at a fresh-gas space velocity of 270 volumes per volume of catalyst per hr.

Occasionally a second-stage operation was installed, using a 5-l laboratory reactor to which was fed about 5 per cent of the tail gas from the pilot plant. The overall conversion in two stages was 92–93 per cent. The space-time-yield in the second stage was about 0.6 kg product per l of catalyst per 24 hr. Usually the catalyst deteriorated measurably after 2 months of operation. Its surface was coated with a material which could be extracted with benzene or xylene, and thereby the catalyst activity was partially restored.

A larger reactor containing 4 cu m of catalyst was built and tested. The catalyst bed was 80 cm thick and was contained in a horizontal cylinder, designed (see Figure 14) for minimum pressure drop. The hot-gas recycle generated steam at 60 atm in a high-pressure coil in the recycle line. To increase the life of the catalyst, a small fraction of the total recycle gas was continuously diverted and passed through a cold-gas recycle to separate the reaction water and high-boiling products.

Operation was started by passing steam at 20 atm through the high-pressure heat exchanger in the recycle line, and the recycle gas was brought to reaction temperature by an electric preheater. The production amounted to about 3 tons of products per 24 hr. After 7–8 weeks of operation the production of methane increased with a corresponding decrease in that of liquid products. One of the thermocouples showed an abnormally high temperature. Operation was stopped, and inspection of the reactor showed a nucleus of soot in the lower part of the catalyst bed near the gas inlet. In the center of this hot spot the cata-

lyst particles were densely packed in carbon and were partially spalled. Obviously, the gas velocity was not uniform through the bed and had been so low at this spot that the expected temperature increase of 10°C had been exceeded, causing carbon deposition and a large yield of methane. It seemed likely that the change in velocity and direction of gas flow at the entrance to the catalyst space caused sufficient turbulence to result in a higher velocity through part of the bed and a very

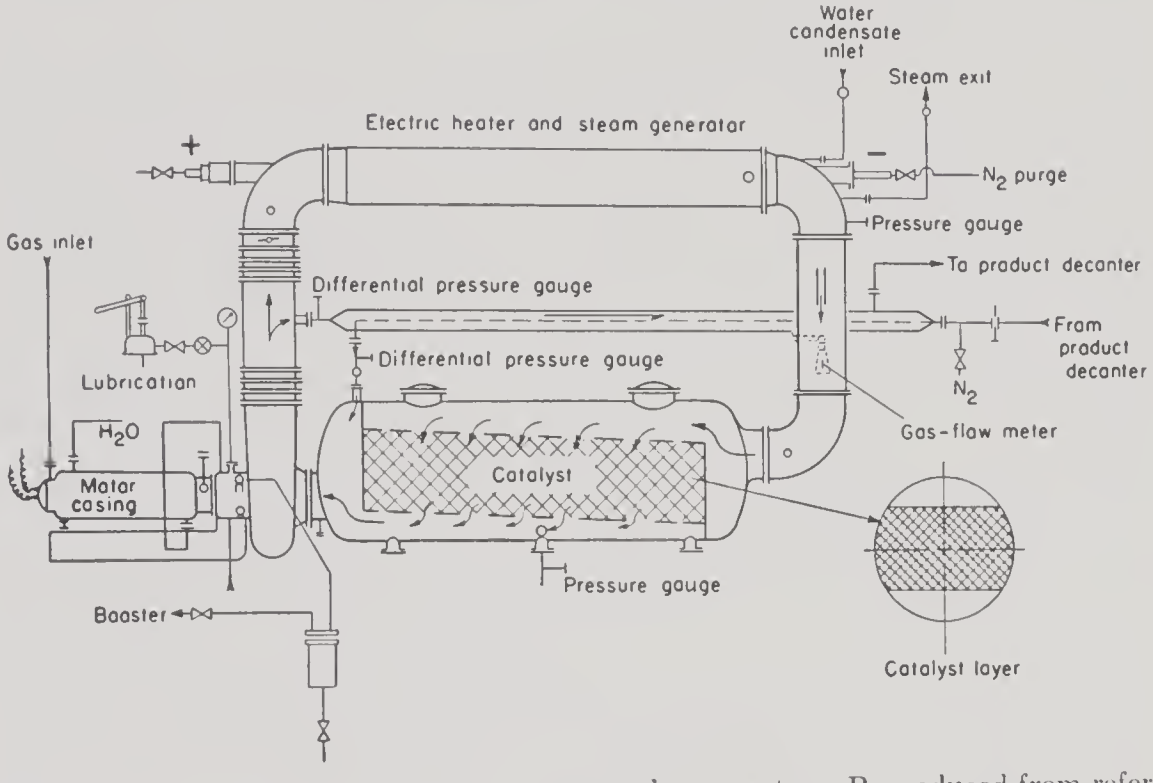


FIGURE 4–14. Four-cubic-meter hot-gas recycle converter. Reproduced from reference 78.

low velocity in the region where the hot spot developed. Baffles were inserted so as to avoid such channeling, and the catalyst bed was divided into three horizontal layers with sufficient gas space between layers to insure a redistribution of gas flow before each layer. Performance was greatly improved by these changes, but again after 2 months' operation there was evidence of a hot spot and soot formation in the part of the catalyst closest to the point of entry of the feed gas.

A redesign of the reactor by Michael,[78] to provide more efficient gas distribution and cooling, is shown in Figure 15. The catalyst and cooling sections are arranged alternately in several layers in series within a vertical cylinder. This design was not tested. Michael was pessimistic about the feasibility of satisfactory operation for more than about 2 months and suggested [78] that arrangements should be made to recharge fresh catalyst at 2-month intervals.

The proximate composition of the products produced in the 400-l converter is shown in Table 44. The data are for two-stage operation with carbon dioxide removal between stages. The unrefined gasoline had a

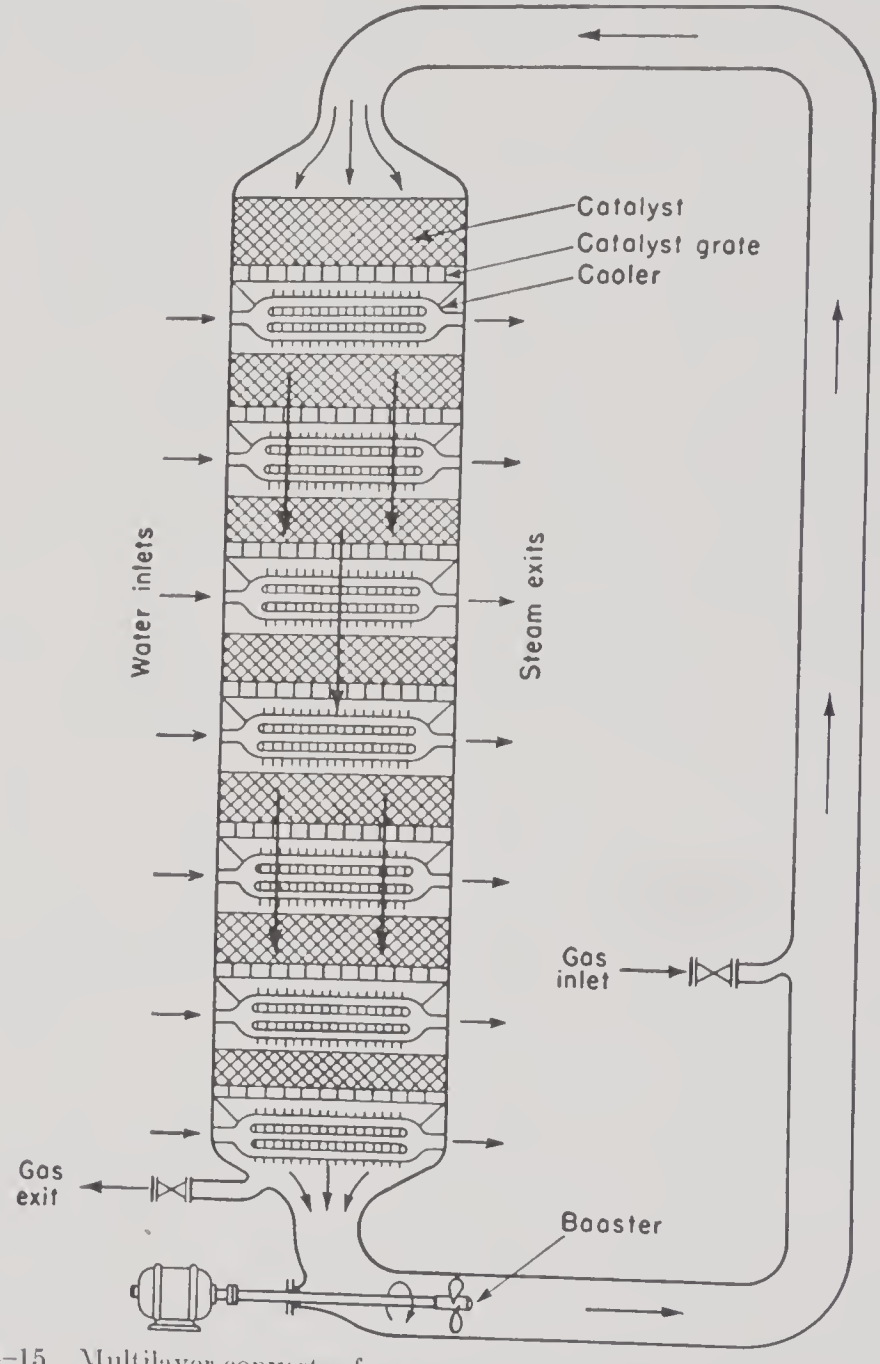


FIGURE 4–15. Multilayer converter for gas recycle, 20 atm. Reproduced from reference 78.

75–81 research octane number, which increased upon refining (passage over bauxite at 300°–400°C) to 84–86. The Diesel oil had a 47–53 cetene number and a minus 25°C pour point. The olefin content of the gasoline was 70 per cent and that of the Diesel oil 50 per cent. The

oxygen compounds in the reaction water contained, in weight per cent, 10 acetaldehyde, 5 acetone, 55 ethanol, 20 propanol, 10 butanol and higher alcohols.

The product composition of Table 44 is very similar to that obtained in the fluidized-iron-catalyst process (see p 430 of this chapter). The

Table 44. Products of I.G. Farben. Hot-Gas-Recycle Process

Constituent	Grams per Cubic Meter of $H_2 + CO$			Composition of Refined Product, weight per cent
	Raw		Refined	
Methane + ethane	35		35	25.5 [a]
Ethylene	10	Polymerization	8	29 gasoline ....
C_3 (70–80 per cent olefin)	17	Polymerization	12	gasoline ....
C_4 (70–80 per cent olefin)	14	Polymerization	11	2 Diesel ....
Gasoline to 200°C	83		78	54.7
Diesel oil, 200°–320°C	21		21	11.8
Wax	1.5		1.5	0.8
Oxygen compounds (chiefly ethanol and propanol)	14		14	7.2
Refinery loss (chiefly as C_1–C_3 saturated hydrocarbons)			15.0	....
Totals	195.5		195.5	100

[a] Includes all C_1–C_3 saturated hydrocarbons.

operating temperatures and pressures are virtually the same for the two processes, and it is significant that the catalyst must be discharged and replaced at frequent intervals in both processes.

THE OIL-RECYCLE PROCESS

The heat evolved in the Fischer-Tropsch synthesis can be efficiently removed by direct heat exchange between the reaction mixture and an oil circulated through a granular bed of catalyst. The heat may be absorbed as sensible heat of the oil, as heat of evaporation of the oil, or by a combination of both conductive and evaporative cooling. This type of operation was developed in 1934–1943 by F. Duftschmid, E. Linckh, and F. Winkler at the I.G. Farben.[78-81] and further by Peck,

[79] T.O.M. Reel 134, Item I-a, No. 8; Item I-b, Nos. 11, 12, 13.

[80] F. Duftschmid, E. Linckh, and F. Winkler, U. S. Patents 2,159,077, May 23, 1939; 2,207,581, July 9, 1940; 2,287,092, June 23, 1942; 2,318,602, May 11, 1943.

[81] M. Pier and W. Michael, U. S. Patent 2,167,004, July 25, 1939.

Atwell, and Sensel [82-84] in the Standard Oil Development Company and the Texas Company.

In most of this development work, a fraction of the oil from the process itself was used as cooling oil. The boiling range of the cooling oil was so chosen that about 50 per cent of the heat of reaction was removed by vaporization of fractions of the cooling oil, and the remainder by sensible heat of this oil. Duftschmid and his coworkers apparently believed that removal of an appreciable part of the reaction heat by evaporation of the cooling oil was essential for successful operation of the process. Later work at the U. S. Bureau of Mines (described below in this section) has shown that it is feasible and probably more efficient to operate with little or no evaporative cooling. The amount of cooling oil per unit weight of oil synthesized increased with decrease in the proportion of evaporative cooling and with decrease in the temperature rise permitted in passage of the oil through the catalyst bed.

Duftschmid [78] presents the following tables (45 and 46), showing the number of kilograms of cooling oil needed per kilogram of oil product for

Table 45. Cooling Oil Necessary for 100 Per Cent Conductive Cooling

Temperature Rise through the Catalyst, °C	Kilograms of Cooling Oil per Kilogram Oil Product
5	1,600
10	800
25	320
50	156

Table 46. Cooling Oil Necessary for Varying Proportions of Evaporative and Conductive Cooling

Per Cent of Heat Removed by Evaporation	Kilograms of Cooling Oil per Kilogram Oil Product for a Temperature Rise through the Catalyst of					
	5°	10°	25°	50°	60°	80°C
10	532	400	230	132	112	87
25	266	280	160	105	92	76
50	145	135	122	79	72	62
75	100	93	80	63	58	51

[82] E. Peck, U. S. Patent 2,161,974, June 13, 1939.
[83] H. V. Atwell, U. S. Patent 2,433,225, Dec. 23, 1947.
[84] E. E. Sensel, U. S. Patent 2,411,760, Nov. 26, 1946.

90 per cent conversion of $1CO + 0.8H_2$ with 2.7 cu m of end gas and 0.23 kg of water formed per kg of oil product. In Duftschmid's experiments the temperature rise through the catalyst bed was about 50°C, and the cooling oil flow into the bed was 40–60 kg per kg of oil product. This is lower than the 79 kg shown in Table 46 for 50 per cent evaporative cooling, and the difference represents heat losses from the converter and

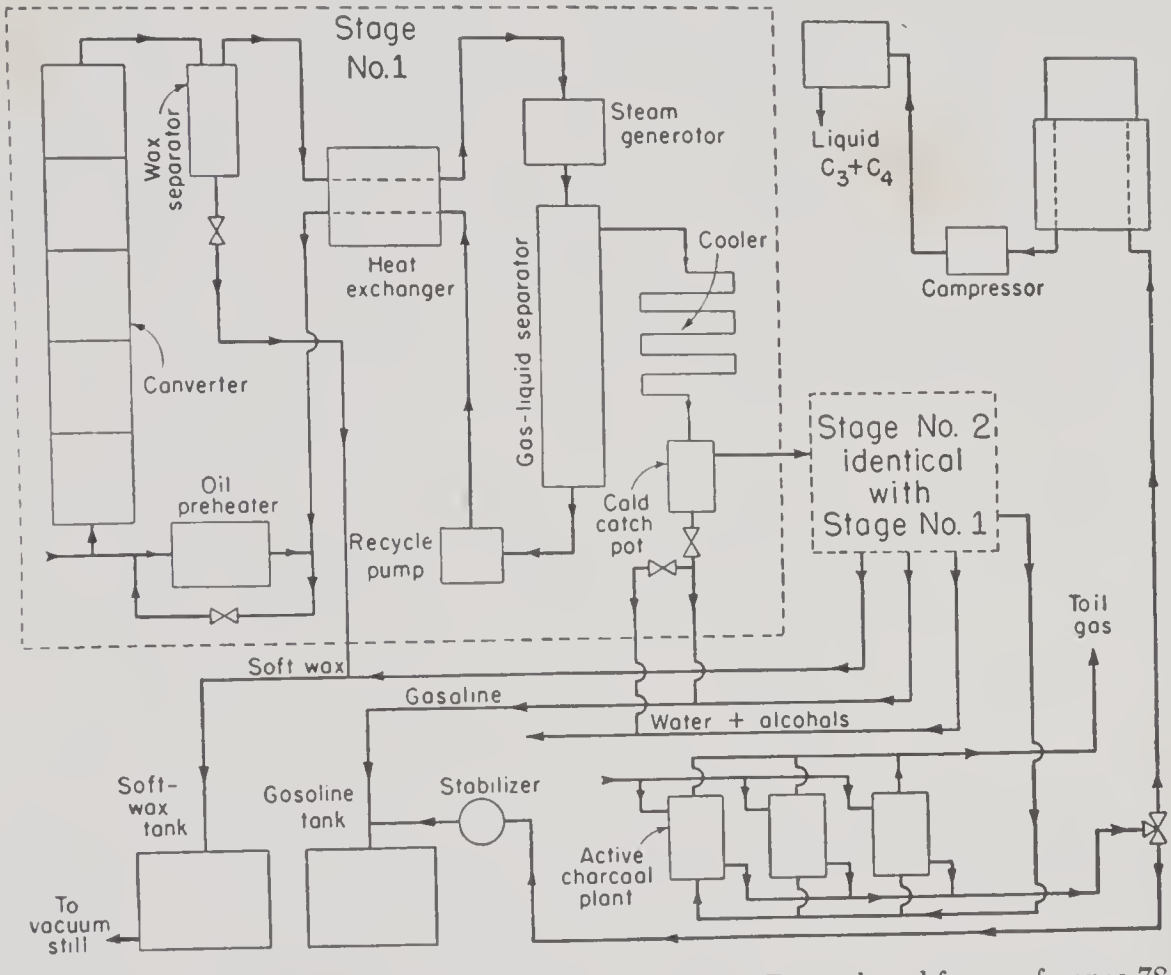


FIGURE 4–16. Flow diagram, oil-circulation process. Reproduced from reference 78.

auxiliary piping, oil pump, etc, to the atmosphere. Figure 16 is a flow diagram for these experiments. The reactors were 50 and 20 cm in diameter, and the height of the catalyst bed was 6 m. The operating temperatures were 240°–290°C in stage 1 and 270°–320°C in stage 2; the pressure, 15–25 atm. The space velocity was about 140 volumes (measured at atmospheric pressure) of $1CO + 0.8H_2$ per volume of catalyst per hour. No recycling of end gas was done in these experiments.

The catalyst (I.G. Farben.-Linckh No. 997) was prepared by mixing 1 kg of iron powder with 25 g of silicon powder, 25 g of titanium dioxide, 50 g of potassium permanganate, and 50 g of water. The mixture was fused in an electric arc, crushed to 4–10-mm size, and reduced. Reduc-

tion was done with carefully dried hydrogen at 450°–500°C and a throughput of 200–300 l per kg of catalyst per hr for 5–6 days. The reduced catalyst after cooling in hydrogen was flushed with carbon dioxide and transferred to the reactor under a blanket of carbon dioxide.

Pilot-plant tests in a 1.5-cu-m converter were done in 1938. The operation was a single-stage test of 5 months' duration, producing 9 tons of hydrocarbons (C_3+) per month. This yield was 8.3 kg per cu m of catalyst per hr. Duftschmid [78] stated:

> The process was thus proved to be practical and safe. The robustness of the catalyst is characteristically indicated by an experiment with the 1.5 cu m reactor in which the catalyst was used without deterioration after the reactor had been in disuse for two years. . . . The second stage operation was operated successfully using a makeshift 200-l converter over a period of one month (unfortunately, a complete two-stage pilot plant was unavailable).

Preheated synthesis gas and recycle oil (boiling range, 3 per cent 150°–200°C, 12 per cent 200°–250°C, 17 per cent 250°–300°C, and 68 per cent above 300°C) passed through the converter from bottom to top in concurrent flow. Exit oil and gas exchanged heat with the cold recycle oil and then passed to a steam boiler from which they emerged at 120°C. At this temperature oil condensable at 120°C was separated and recycled to the reactor. The gases and vapors not condensed at 120°C were cooled to room temperature, and an aqueous layer and an oil layer were obtained in the cold catch pot. When operated in two stages the end gas from the cold catch pot was, according to Duftschmid,[78] passed to the second stage, which was similar to the first. After the second stage, either the tail gas was reduced almost to atmospheric pressure and passed through the activated-charcoal plant, or it was passed at operating pressure to an oil scrubber for recovery of gasoline vapors and C_3 and C_4 gases.

In the curves of Figure 17 Duftschmid [78] shows the temperature and conversion gradients through the reactor. It is apparent that the bottom half of the catalyst converted much less $CO + H_2$ than the top half. Indeed, in the top meter of the catalyst about one-half of the total (50 per cent) conversion occurred. To remedy this poor utilization of the lower half of the catalyst bed, Duftschmid proposed to increase the height of the catalyst to 9 m and introduce part of the cooling oil at about the middle of the catalyst bed. He suggested that with an 18-m height of catalyst bed 90 per cent conversion may be obtained in one stage. He stated:

> Whether the single- or two-stage operation is more economical in full-scale operation cannot be decided by us. When testing a two-stage operation with a

total conversion of 75 per cent, the specific yield in the second stage was 140 to 150 g (per cu m of $1CO + 0.8H_2$ reacted) whereas 165 to 170 g were obtained in the first stage (at 50 per cent conversion).

The Synthetic Liquid Fuels Research and Development Branch of the Bureau of Mines, U. S. Department of the Interior, has been doing development work on the oil-circulation process since 1944.[85]

A typical flow diagram is given in Figure 18. Synthesis gas, recycled end gas, and circulated cooling oil are passed concurrently upward

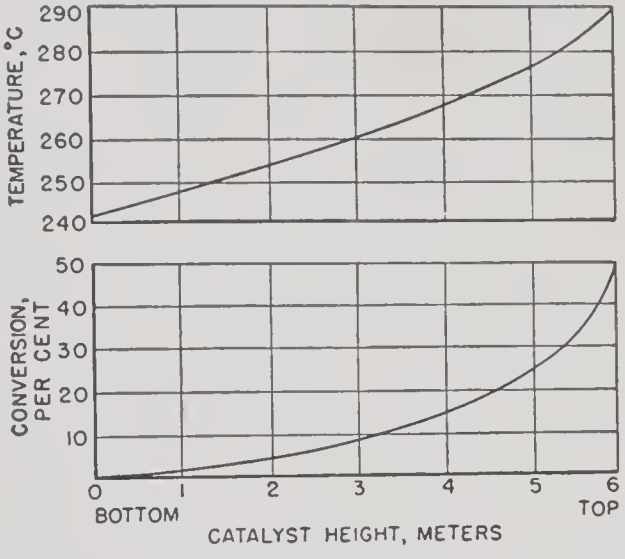


FIGURE 4–17. Temperature and synthesis gas conversion gradients in Duftschmid's oil-circulation reactor. Reproduced from reference 78.

through a bed of catalyst granules. The cooling oil is separated from the gases and vapors and recycled. In the early experiments both granular and pelleted precipitated iron catalysts were used and found quite active. After a short period of operation, however, these catalysts crumbled because of hydraulic erosion by the cooling oil. Subsequently a fused magnetite catalyst containing suitable promoters was used. Although less active than precipitated iron catalysts, the fused magnetite has a high crushing strength and is not disintegrated by hydraulic erosion. A cooling oil boiling in the range 300°–450°C at atmospheric pressure is used, so most of the heat of reaction is removed as sensible heat of the oil, rather than by heat of vaporization. The cooling oil circulation rate is adjusted so that the increase in cooling oil temperature during passage through the catalyst bed is only about 15°C. A cold-gas recycle is em-

[85] J. H. Crowell, H. E. Benson, J. Field, and H. H. Storch, *Fischer-Tropsch Pilot-Plant Studies of Oil Circulation Processes at the U. S. Bureau of Mines*, presented at the 117th National Meeting of the American Chemical Society, Houston, Texas, March 26–30, 1950. To be published in *Ind. Eng. Chem.*

ployed so that water formed in the synthesis is condensed and not recycled.

Several pilot-plant tests of 1–3 months' duration were made, using 2–4 and 4–6 mesh fused catalyst containing 93.5 per cent Fe_3O_4, 4.6 per

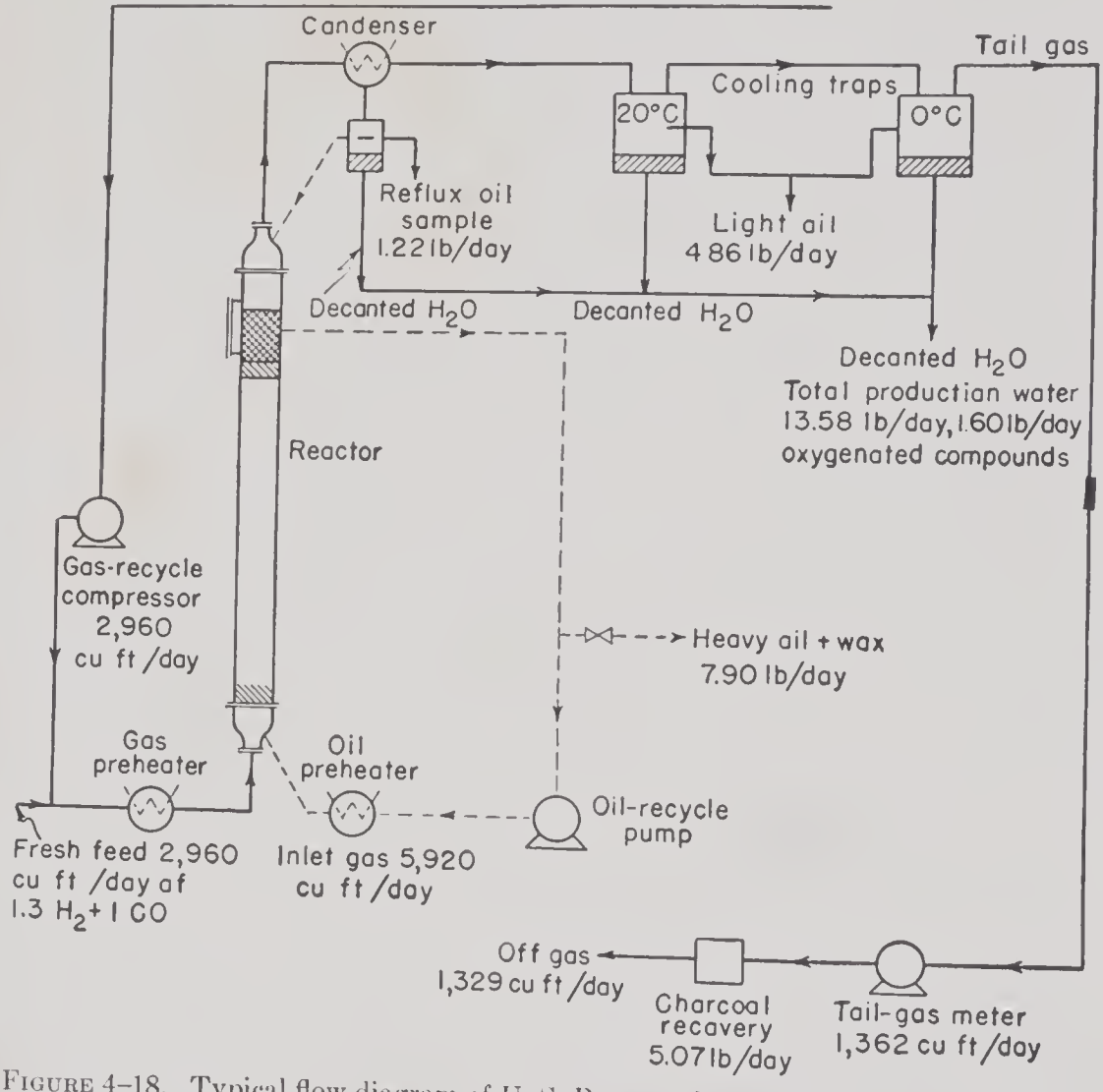


FIGURE 4–18. Typical flow diagram of U. S. Bureau of Mines oil-circulation process. Reproduced from reference 85.

cent MgO, 0.65 per cent Cr_2O_3, 0.05 per cent Mn_3O_4, 0.6 per cent K_2O, and 0.6 per cent SiO_2. The catalyst was virtually completely reduced at 450°C by passage of 2,000 volumes per hour of dry recycled hydrogen per volume of catalyst until water formation ceased. After the reduction, the catalyst was cooled in a hydrogen atmosphere. The hydrogen was displaced by CO_2 and the catalyst was discharged and stored under a CO_2 atmosphere until ready for use. Synthesis was started after a 4-day induction period during which the conversion of synthesis gas was increased in a step-wise fashion by increasing the catalyst tem-

perature while the pressure, fresh-gas feed rate, and end-gas recycle ratio were held at their normal operating values. Most experiments were run at 300 fresh-feed space velocity (volumes of fresh feed at NTP per hour per volume of catalyst) and 70 per cent synthesis gas conversion. The gas-recycle ratio (volumes of end gas per volume of fresh gas) was varied to adjust the H_2:CO use ratio as closely as was practical to that of the feed gas, so that the second stage of the synthesis would operate with gas having the same H_2:CO ratio as that fed to the first stage. It was found necessary to terminate the synthesis after 2–3 months, even though the catalyst was still active, because the pressure drop across the catalyst bed had risen from its initial value of 5 psi to 35 psi. This high-pressure differential greatly increased the power required for circulation of the cooling oil and of end gas. On inspection, the catalyst particles were found to be tightly cemented together, and the catalyst bed had to be drilled and chiseled to remove it from the reactor.

Among other changes made to alleviate this difficulty, the H_2:CO ratio in the fresh feed gas was increased from 1:1 to 1.3:1. Use of the $1.3H_2$:1CO feed gas reduced the rate of increase of the pressure drop. An increase from 5 to only 15 psi was observed during 3 months of operation, as compared with 35 psi under otherwise identical conditions with $1H_2$:1CO feed gas. Even with $1.3H_2$:1CO gas, however, the catalyst particles again were found cemented together. To solve the problem of catalyst cementation, a smaller particle size of catalyst was used, and the cooling oil was circulated at a sufficiently high rate to expand the catalyst bed by about 25–35 per cent of its settled volume and to keep the catalyst particles in continuous, agitated motion. The linear velocity of the cooling oil required to produce this motion in a bed of 8–16 mesh fused magnetite catalyst was 0.10–0.15 ft per sec. Several satisfactory pilot-plant runs employing the moving catalyst bed were made, and although some reduction in particle size of the catalyst occurred after a period of time, only a negligible amount of finely divided catalyst was present in the cooling oil recycle. Moving-bed operation was superior to fixed-bed synthesis not only because catalyst cementation was prevented, but also because the use of the smaller catalyst particles provided greater catalyst activity. For example, in fixed-bed operation using 54 lb of 4–6 mesh fused catalyst, an average operating temperature of 248°–258°C was required for 70 per cent conversion of 124 cu ft (NTP) per hr of $1.3H_2$:1CO gas. For the same conversion in a moving bed with 27 lb of the same catalyst of 8–16 mesh, a temperature of only 240°–245°C was necessary. Thus, even though twice the amount of gas was converted per pound of catalyst in the moving bed, a 10°C lower temperature prevailed. The advantages of the moving-bed operation

over the fixed beds are (1) greater facility of operation, including ease of replacing used catalysts; (2) use of a lower operating temperature with the probability of lower C_1, C_2, and $C_2=$ specific yields (see Table 47); (3) greater synthesis gas conversion per pound of catalyst, resulting in material reduction of catalyst cost.

Typical operating and yield data are presented in Tables 47 and 48 for

TABLE 47. U. S. BUREAU OF MINES OPERATING DATA FOR THE OIL-CIRCULATION PROCESS

(3 in. by 10 ft reactor, 20 atm, Fe_3O_4-MgO-Cr_2O_3-MnO-SiO_2-K_2O-93.5:4.6:0.65:0.5:0.6:0.6 fused catalyst. Fresh feed gases contained 0.5 per cent or less of inerts.)

Run number	14	17	19
Catalyst bed	Fixed, 8 ft, 4–6 mesh	Fixed, 8 ft, 4–6 mesh	Moving, 5.2 ft, 8–16 mesh
Maximum temperature, °C	254–265	255–265	244–249
Temperature differential, °C	16	15	6
H_2:CO ratio of feed gas	1:1	1.3:1	1.3:1
Hourly space velocity (volumes of gas per hour per volume of catalyst)	300	302	462
Fresh feed-gas rate [a]	124.5	124.2	123.2
Gas recycle ratio	2:1	1:1	1:1
H_2 + CO conversion, per cent	69.9	70.0	70.3
H_2:CO use ratio	1:1	1.1:1	1.04:1
C_1 + C_2, g per cu m feed gas	24.5	26.3	21.9
C_3+, g per cu m of feed gas [b]	99.9	108.8	117.2

[a] Standard cubic feet per hour.

[b] Values have been corrected for theoretical removal of oxygenated groups by bauxite or similar treatment without losses.

TABLE 48. PRODUCTS [a] OF U. S. BUREAU OF MINES OIL-CIRCULATION PROCESS

(Grams per cubic meter of feed gas at 70 per cent conversion.)

Run number	14	17	19
Methane	13.3	13.9	10.3
Ethane	9.2	10.2	7.6
Ethylene	2.0	2.2	4.0
Gasoline [b] (to 204°C)	71.9	72.5	73.2
Diesel oil (204°–316°C)	11.3	12.3	13.4
Fuel oil (316°–450°C)	8.0	13.8	15.6
Wax (>450°C)	8.7	10.2	15.0
Oxygenated compounds in water layer	15.0	11.3	8.6

[a] Oxygenated groups in the oil streams are deducted. No losses are assumed except for the weight of these groups.

[b] Includes C_3 and C_4.

fixed-bed operation with 1:1 and 1.3:1 H_2:CO feed gas, and for moving-bed operation with 1.3:1 H_2:CO feed gas. Data have not yet been obtained for the use of 1:1 H_2:CO feed gas in the moving bed.

In general, the product distribution from the fixed and agitated beds were alike except for the somewhat lower total yield of the $C_1 + C_2$ components in the moving bed. Properties of the gasoline and Diesel oil were about the same for the two types of operation. The gasoline fractions had bromine numbers of 50–60, and the antiknock octane rating of the untreated gasoline was 65 (motor method). The Diesel fraction had a cetane rating of 78.

During run 19 the conversion was decreased to 50 per cent by lowering the hourly space velocity to 230 and the temperature to 219°C. Under these conditions the $C_1 + C_2$ yield dropped to 16.0 g per cu m of fresh feed gas. In another experiment during run 19 the end-gas-recycle ratio was increased to observe the effect on the H_2:CO use ratio and on the $C_1 + C_2$ yields. The results are given in Table 49. Table 49 shows

TABLE 49. USE RATIO AND $C_1 + C_2$ YIELD AT DIFFERENT END-GAS-RECYCLE RATIOS IN U. S. BUREAU OF MINES OIL-CIRCULATION PROCESS

(3 in. by 5.2 ft moving bed of 8–16 mesh catalyst, hourly space velocity 230 volumes of fresh gas per volume of catalyst. Conversion of $1.3H_2 + 1CO$ was 70 per cent.)

Recycle Ratio, End Gas:Fresh Gas	Temperature, °C	CO_2 in End Gas, per cent	Use Ratio, H_2:CO	$C_1 + C_2$, g per cu m of H_2 + CO converted [a]
1	238	27.4	0.99	30.7
2	233	25.1	1.03	31.6
3	232	23.4	1.15	29.8
4	231	22.9	1.13	26.0
5	232	21.5	1.15	22.5
6	233	20.3	1.22	20.3
7	231	21.5	1.21	24.0
1	238	26.6	1.02	30.6

[a] The data in this column must be multiplied by 0.70 to compare them with the corresponding data in Tables 47 and 48.

that, when an end-gas- to fresh-gas-recycle ratio of 6 was used, a maximum H_2:CO use ratio of 1.22 and a minimum of 20.3 g of $C_1 + C_2$ per cu m of H_2 + CO converted were obtained. The development work on this process has not yet been completed. A careful study of catalyst preparation and of induction procedures is in progress.

Processes Using Suspensions of Powdered Catalysts

LIQUID-PHASE SUSPENSIONS

In 1935 the Ruhrchemie and the Gewerkschaft Viktor in Germany conducted some tests, using a suspension of cobalt catalyst in oil for the Fischer-Tropsch synthesis.[86, 87] A high rectangular tower was used. The heat of reaction was removed by water-cooled tubes uniformly distributed through the converter. The flow of the synthesis gas was either concurrent or countercurrent to the flow of the catalyst-oil suspension. The initial results were fairly promising, but after a short time methane formation increased rapidly because of settling of catalyst on the cooling tubes.

From 1939 to 1944 additional laboratory and pilot-plant work with liquid-phase suspensions was done at Rheinpreussen, Ruhrchemie, and I.G. Farben. At Rheinpreussen most of the experimental work [88, 89] was done in reactors 5 cm in diameter by 350 cm high, containing a porous ceramic disc at the bottom for gas distribution. The liquid vehicle usually was the Diesel oil fraction from the Ruhrchemie-type, cobalt-catalyst, commercial process. Unfortunately, none of the tests was of sufficient duration to replace this vehicle by one characteristic of the liquid-phase catalyst-oil suspension process. A number of interesting facts, however, were disclosed by the Rheinpreussen experiments. The catalyst used in these tests was prepared by precipitation with sodium carbonate from ferric nitrate plus copper nitrate solutions. After filtration and washing, the catalyst was impregnated with a dilute potassium carbonate solution, and the paste was then dried and ground to about 50-micron particle size. Its composition was approximately $100Fe:0.5Cu:0.7K_2O$ (weight ratio). About 12 per cent by weight of catalyst powder was added to the oil vehicle, and 5 kg of the mixture was put into the reactor. The best results were obtained by pretreating the catalyst-oil suspension with pure carbon monoxide at 2 atm for 9 hr before starting the synthesis. The oil-catalyst suspension was first heated to 200°C while passing 100 l of nitrogen per hr through it; then the nitrogen flow was replaced by a flow of 200 l of carbon monoxide per hr at 2 atm pressure; the temperature was increased to 270°C in 4 hr and maintained at 270°C for an additional 5 hr. The temperature then was

[86] Appendix to reference 75, comments by L. Alberts.
[87] F.I.A.T. Reel K22, Frames 1,177–84.
[88] F.I.A.T. Reel 115-X, Frames 1,388–447, 1,593–672.
[89] C. C. Hall, S. R. Craxford, D. Gall, and S. L. Smith, PB 91,925 (1948); *B.I.O.S. Final Rept.* 1,712 (*Interrogation Rept.* 679, Item 30).

lowered to about 200°C, and the carbon monoxide replaced by water gas ($1.28H_2$:1CO) at 10 atm. With a flow of about 7.5 l (at atmospheric temperature and pressure) of water gas per 10 g of iron per hr, an appreciable conversion was obtained at 200°C. Upon increasing the temperature to 219°C during 15 hr, the conversion of carbon monoxide rose to 87 per cent. After 20 hr, when a temperature of 225°C was reached, the temperature could be lowered to 212°C without decreasing the conversion below 88 per cent. Operation in one stage was conducted for 140 hr at the temperatures and CO conversions shown in Table 50.

Table 50. Rheinpreussen Single-Stage Operation in Liquid Phase at 10 atm of $1.28H_2 + 1CO$ Feed Gas

Temperature, °C	194	232	231	219	220	222	221	222
Operating time, hr	3	15	20	40	60	80	100	140
Gas flow, normal liters per 10 g Fe per hr	5.0	7.1	8.0	7.0	6.7	7.2	7.0	8.4
CO conversion, per cent	...	88	94	92	87	88	89	89

After two reactors had been operated as a single stage for 140 hr, they were connected in series and a two-stage operation conducted for an additional 70 hr. The end gas from the first stage was cooled to 15°C at 10 atm before passage to the second stage. Data for the two-stage operation are given in Table 51. At 89 per cent CO conversion in the single-

Table 51. Rheinpreussen Two-Stage Operation in Liquid Phase at 10 atm of $1.28H_2 + 1CO$ Feed Gas

Operating Time, hr	Temperature, °C		SVH [a] 1st + 2d Stages, normal liters per liter of reactor volume per hour	Gas Feed 1st + 2d Stages, normal liters per 10 g iron per hour	CO Conversion, per cent		H_2:CO, Use Ratio, 1st + 2d Stages	C_5+, g per cu m feed gas
	Stage 1	Stage 2			Stage 1	Stages 1 + 2		
8	228	225	36	5.7	69	96.2	0.72	147
14	228	224	58	8.0	49	89.5	0.75	143
31	235	232	34	5.6	52	95.5	0.79	145
52	239	237	105	20.5	50	91.8	0.89	156
63	240	236	101	19.8	51	93.0	0.88	157

[a] Apparently the reactor was about one-half filled with the oil-catalyst suspension. It also appears as if the amount of catalyst in the reactor varied with the space velocity because the data of this column would otherwise be inconsistent with those of the next one (gas feed rate per 10 g Fe per hr).

stage test (Table 50) the H_2:CO use ratio was 0.63 and the specific yield 138 g of C_5+ per cu m of water gas. In the first few hours of the two-stage operation (Table 51) at 96 per cent CO conversion, the H_2:CO use ratio was 0.72 and the specific yield of C_5+ was 147 g per cu m. After 50 hr the space velocity was increased about three-fold and the temperature raised to maintain 92–93 per cent conversion. The H_2:CO use ratio increased to 0.88 and the specific yield to 157 g per cu m of water gas. The space-time-yield at 50–60 hr was about 14 kg C_5+ per cu m of catalyst per hr. Rheinpreussen reports that virtually no methane was produced in its experiments. The Diesel oil used as vehicle was found to partake in the synthesis, being converted to wax. Complete hydrogenation of olefins in the Diesel oil before its use as vehicle did not decrease its rate of conversion to wax.

During the period 1945–1948, Kölbel of Rheinpreussen continued development of the slurry process, and in September 1948 he presented some of the results at a meeting in Hannover of the Society of German Chemists in the British Zone. Catalyst preparation was only briefly outlined, with no specific statements concerning the important factors. Hydrated iron oxides were obtained by mixing sodium carbonate solutions with iron nitrate solutions. Small amounts of copper and alkali were included in the catalyst. The dried and powdered catalyst was mixed with a fraction of the synthesis oil boiling in the range 270°–330°C, so as to obtain 50–200 g of iron per l of slurry. Pretreatment, *ie*, reduction with hydrogen or reduction and carbiding with synthesis gas, was barely mentioned and no details given of the procedure actually used. From the data in captured German documents on Kölbel's work during 1943–1944,[72,73] it appears likely that he was using the catalyst 100Fe:5Cu:20MgO:0.5K_2O:50 kieselguhr, pretreated at about 300°C with $2H_2 + 1CO$ gas at about 2,000 hourly space velocity, for 6 hr.

Kölbel stated in his 1948 paper that the flow of synthesis gas was in the range 7–17 l per 10 g of iron in the slurry, for 90–95 per cent conversion of CO in a single stage. This is 2–4 times the flow normally used in the Ruhrchemie process using a "dry" bed of iron catalyst. The operating temperature in Kölbel's slurry tests was 10°–15°C higher than in "dry"-bed tests with the same catalyst. The operating pressure was in the range 5–20 atm, but all pilot-plant data presented by Kölbel were obtained at 10 atm.

The reactor was a cylinder 20 cm I.D. and 6 m high, and contained four cooling bayonets 4.8 cm O.D. connected to a steam drum. Synthesis gas entered at the bottom of the reactor and was distributed by a porous plate. The off gases and vapors from the reactor passed through a partial condenser to liquefy oil boiling above 270°C. Part of this con-

densate was returned to the reactor. Further cooling of the off gas and product vapors was followed by exposure to active charcoal. A stream of high-boiling product was continuously removed from the reactor so as to maintain a vehicle of constant boiling range.

Kölbel presented the data contained in Table 52 to illustrate operating

Table 52. Slurry-Phase Operation with Different H_2:CO Ratios in the Synthesis Gas

	CO-Rich Gas	Water Gas		H_2-Rich Gas
		a	*b*	
H_2:CO ratio in fresh gas	0.64	1.2	1.2	1.95
Use ratio, H_2:CO	0.60	0.89	1.05	1.43
Temperature, °C	252	238	230	226
Number of stages	1	2	1	1
End-gas to fresh-gas recycle ratio	0	0	2.5	1.5
Hourly space velocity [a]	150	105	245	240
Per cent CO conversion	94	93	95.5	95
Yield, g per cu m of CO + H_2				
a. Above C_1	172	157	168	163
b. Methane	6	0	0	0

[a] Probably refers to total feed gas.

conditions with synthesis gas of different H_2:CO ratios. By recycling 1–3 volumes of end gas per volume of fresh synthesis gas it is possible to bring the H_2:CO use ratio closer to the H_2:CO ratio in the fresh feed gas.

In Table 53, Kölbel's data for a 143-day operation in the slurry phase are presented. The stated operating conditions were: pressure, 10 atm;

Table 53. 143-Day Operation of Slurry-Phase Pilot Plant

Time, days	Synthesis Temperature, °C	Liters of Synthesis Gas per 10 g Fe per hr	CO Conversion, per cent	Product Distribution			
				Fraction	g per cu m of CO+H_2 Reacted	Weight Per Cent	Olefins, Per Cent
1	271	10	95	C_1	6	3.4	
110	251	10	90	$C_3 + C_4$	33	18.8	56
120	253	11	93	35°–200°C	91	52.0	45
130	254	15	95	200°–320°C	35	20.0	28
143	251	17	90	Above 320°C	9	5.2	..

H_2:CO ratio in synthesis gas, 0.64; single stage, no recycle of end gas; gas flow, 15 cu m per hr; iron content of slurry, 10 kg per 100 l; slurry bed height, 600 cm. After the first day of operation, catalyst activity was constant during almost 5 months. No catalyst regeneration was necessary during this period. The product contained surprisingly little wax, about 6 per cent. The total yield of oil plus gaseous hydrocarbons was 175 g per cu m of $H_2 + CO$ reacted. The yield of C_2 is not stated, but appears to be 4 g per cu m of $H_2 + CO$ reacted or 2.2 per cent of the total product. No data are given on the oxygen content of the oil or on the amount of water-soluble oxygen compounds.

Ruhrchemie [87, 90] started tests on iron catalyst in liquid-phase suspension in 1940. Most of the experiments were done using tubes 10–15 cm in diameter and 6 m in height, containing a suspension of powdered 100Fe:5Cu:10CaO:100 kieselguhr in Diesel oil. In the early tests the synthesis gas was passed through a porous ceramic plate to obtain good distribution, and uniformity of catalyst suspension in oil was accomplished by pumping the slurry through a side tube from the top to the bottom of the reactor. In later tests the porous gas distributor was replaced by a small-bore tube, and uniform suspension of catalyst was achieved by substituting end-gas recycle for slurry recycle.

The per cent of conversion of carbon monoxide at different flow rates of $1.3H_2 + 1CO$ gas and at various concentrations of catalyst in the slurry is shown in Table 54. A recycle ratio of 3 volumes of end gas per volume of fresh gas was used in all the tests. The volume of catalyst (first column of Table 54) is the volume of the dry granules (before grind-

Table 54. Ruhrchemie Single-Stage Liquid-Phase Tests Using 100Fe:5Cu:10CaO:100 Kieselguhr at 250°C, 15 atm, $1.3H_2 + 1CO$ as Fresh Feed Gas, Recycle of 3 Volumes of End Gas per Volume of Fresh Gas

Volume of Catalyst, liters	Grams of Catalyst per Liter of Oil	Fresh Gas Rate, per hour		Per Cent Conversion of CO
		Liters per Liter of Slurry	Liters per 10 g of Iron	
10	200	18	1.8	73–75
10	200	27	2.7	62–64
10	200	36	3.6	48–52
20	445	36	1.6	73–75
20	445	51	2.3	62–64
20	445	72	3.2	48–53
30	750	51	1.4	70–75

[90] F.I.A.T. Reel No. K-31, Frames 1,108–15.

ing) which are mixed with enough oil to fill the reactor (volume 55 l). For 10 and 20 l of catalysts, about 50 and 45, respectively, of oil were necessary. For an assumed bulk density of the catalyst granules of about 1, the concentrations in the second column were calculated from the data in the Ruhrchemie report. The catalyst probably was reduced with hydrogen before grinding and mixing with the oil, although no mention is made of reduction in the Ruhrchemie report of these tests. The fresh-gas space velocity (third column of Table 54) for about 70 per cent CO conversion is very low compared with that of the granular-bed oil-circulation process (p 407 of this chapter). The low space-time-yield of the Ruhrchemie catalyst is partly due to the appreciably lower pressure of 15 atm, as compared with 20–25 atm in the oil-circulation process, and to the lower activity of the catalyst.

Table 55 contains the results of a two-stage liquid-phase operation by Ruhrchemie. Although the amount of catalyst per liter of slurry is not specified, it may be inferred, by comparison of the CO conversions and space velocities of Tables 54 and 55, that both stages contained about 445 g of catalyst per l of oil.

The off gas from the reactor in each stage was cooled to room temperature, thus condensing all Diesel oil, wax, and a fraction of the gasoline and water. From the condenser the off gases passed to the active charcoal scrubbers. The oil condensed by cooling was separated from the water and returned to the reactor. A constant oil level was maintained in the reactor by withdrawing oil periodically through a filter stick immersed in the oil-catalyst slurry. After 2–3 weeks of operation, the composition of the vehicle reached a steady state characteristic of the operation. Ruhrchemie's longest time of operation in liquid phase was $7\frac{1}{2}$ weeks. Actual product recovery was incomplete. The yield of C_3+ calculated from gas analysis was about 170 g per cu m of $H_2 + CO$ reacted and about 155 g per cu m of inert-free fresh gas. Methane production increased from about 2 per cent of the CO reacted at the start to about 6 per cent at the end of the $7\frac{1}{2}$-week period of operation. Addition of 750 g of soda dissolved in Diesel oil to the slurry increased the wax production and decreased the H_2:CO use ratio. Addition of 5 l of C_{10}–C_{18} fatty acids increased the H_2:CO use ratio to 1.8, but this decreased after a short time to about 1.1. Methane production increased to about 9 per cent after the addition of the acid.

At I.G. Farben. pilot-plant tests [78] on the liquid-phase process were started in 1940. A 250-l converter 20 cm in diameter and 380 cm in height was used. A motor-driven (900 rpm) stirrer was placed in the lower section of the reactor. About one-half of the reactor volume contained oil-catalyst slurry. The stirring resulted in a parabolic liquid

TABLE 55. RUHRCHEMIE TWO-STAGE LIQUID-PHASE OPERATION WITH 100Fe:5Cu:10CaO:100 KIESELGUHR CATALYST IN 55-l REACTORS, USING $1.3H_2 + 1CO$ FRESH FEED GAS

	Stage 1				Stage 2				Total			
Time of operation, hr			833				732				....	
Temperature, °C			250				252				....	
Pressure, atm			15				15				....	
Gas rate, cu m per hr			3.1				1.33				....	
Recirculation ratio			2				3				....	
Residual gas analyses, per cent												
CO_2			24.7				48.3				....	
C_nH_m			1.6				1.8				....	
CO			27.8				10.8				....	
H_2			30.0				12.6				....	
CH_4			2.1				5.6				....	
N_2			13.7				21.2				....	
Contraction, per cent			50.2				35.5				67.3	
Conversion of	CO	H_2	$CO + H_2$		CO	H_2	$CO + H_2$		CO	H_2	$CO + H_2$	
Volume per cent	64.0	69.3	69.4		75.0	73.2	74.0		91.0	91.6	91.2	
CO converted to	CO_2	CH_4	C_3+		CO_2	CH_4	C_3+		CO_2	CH_4	C_3+	
Per cent of CO reacted	25.0	3.3	71.7		31.3	6.3	62.4		27.6	4.3	68.1	
Use ratio, H_2:CO		1.36				1.05				1.28		
Yield of C_3+, g per cu m of $H_2 + CO$ reacted		126				93				170		
Boiling range, °C	To 200	200–320	320–460	Above 460	To 200	200–320	Above 320		To 200	200-320	320–460	Above 460
Volume per cent of C_5+	18.4	21.9	26.6	32.1	50.3	30.1	18.3		24.9	29.8	21.6	23.6
Boiling range, °C	To 200			200–320	To 200		200–320		To 200			200–320
Olefin + oxygenated compounds												
Volume per cent of fraction	63			21	78		5		65			17

surface, the liquid level in the center being only a little above the stirrer, while the level at the walls was just below the top of the reactor. Feed gas (100 cu m per hr of $1H_2 + 1CO$) was conducted into the axial gas space and was very efficiently distributed as small bubbles in the slurry by the mechanical agitation. Besides experiencing difficulties with the packing on the stirrer shaft, sedimentation of the catalyst on different parts, especially on the converter wall just above the slurry level, resulted in hot spots, catalyst deterioration, and excessive methane production.

Most of I.G. Farben.'s laboratory and pilot-plant development work [78, 91] on the liquid-phase process was done using porous ceramic plates located at the bottom of cylindrical reactors for gas distribution. These plates were made by sintering powdered quartz, with glass as a binder, to form a hollow cone with walls 4–5 mm thick. The diameter of the pores was 0.1–0.15 mm. A thin foil of asbestos served as gasket, and a heavy iron grid above the porous plate retained it in position.

Laboratory-size reactors were 300 cm high with slurry volumes of 3, 10, and 25 l. They were double tubes with "gas-lift" recirculation of the slurry through the central tube. The gas bubbles from the porous ceramic plate rose through the annular part of the reactor, which resulted in a lower slurry density in the annulus than in the central tube. Semi-technical-scale reactors contained 300 l of slurry and were equipped with a slurry-recycle pump. A typical flow diagram is presented in Figure 19. Also, a larger semi-technical-scale reactor containing 1.5 cu m of slurry was tested. It was 50 cm in diameter and 8 m high, and the gas separator had a volume of 600 l. The cross-sectional area of the slurry-recycle line was about 5 cm.

The catalyst was prepared by first burning iron carbonyl to form iron oxide. This was then mixed with a dilute potassium borate solution in water so as to provide about 1 part of K_2O per 100 parts of iron. The resulting paste was dried, crushed to a convenient-size granule, and completely reduced with dry hydrogen. After cooling in hydrogen, and displacing the hydrogen with carbon dioxide, the granules were submerged in middle oil and finally ground in a ball mill as finely as possible (a particle size of about 2 microns is reported). The reactor was charged with a slurry containing 150–300 g of reduced catalyst per l. The vehicle was that from a previous operation, or, when starting the reactor for the first time, paraffin wax was used. The H_2:CO ratio in the feed gas was 0.8. Operating temperatures were in the range 240°–275°C.

[91] Translation Nos. 431, 432, 438 of documents from Dr. Pier's files, by W. M. Sternberg, Office of Synthetic Liquid Fuels, U. S. Bureau of Mines, Louisiana, Mo.; T.O.M. Reel 274, Frames 1,437–98.

After 2 months of operation of the 1.5-cu-m reactor a marked decrease in catalyst activity and irregularities in temperature gradients in the reactor were observed. Upon opening the reactor, a ring-shaped, crumbly cake of virtually dry catalyst was found on the upper section of the reactor wall. The thickness of this layer was greatest on the wall of the top section, and it gradually decreased until, close to the porous

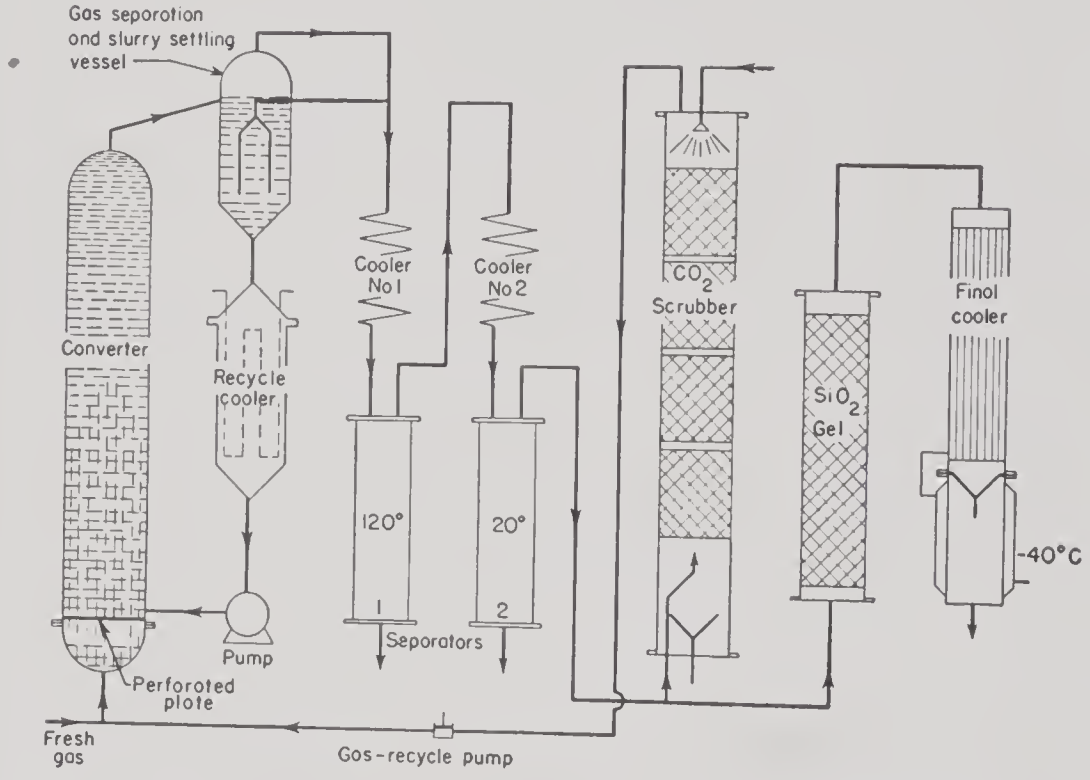


FIGURE 4–19. Flow sheet of liquid phase with recycle. Reproduced from reference 78.

ceramic plate in the bottom section of the vessel, no deposit was observed. Similar deposits were observed in the gas separation vessel. These deposits consisted mainly of FeO and Fe_2CO_3, which are stable in gases containing appreciable proportions of CO_2 and H_2O, such as the off gas from a 70 per cent conversion in a single pass through the reactor. A scraper rotating slowly around the wall was then installed to keep the walls clean. After 3 additional months of operation the walls were free of scale, but the scraping equipment itself was covered by a thick scale, parts of which dropped onto the porous ceramic plate and adversely affected the gas distribution. Plans for further development were: first, to test converters of smaller height, operating with a lower degree of conversion per pass so as to avoid high percentages of CO_2 and H_2O; second, to use hydrogen-rich synthesis gas which would further reduce the CO_2 concentration and which might hydrogenate any "gum-

formers" that might have assisted in forming the scale; third, to pass a small portion of the slurry recycle over a solid absorbent to remove resinous compounds of high molecular weight.

In 1942–1943, Dr. W. Michael of the I.G. Farben. presented the following data [78, 91] for operation of the 1.5-cu-m reactor:

Synthesis gas: H_2:CO ratio 0.8–0.75; inerts did not exceed 1–2 per cent, sulfur was less than 2 mg per cu m.

Catalyst: was made from iron carbonyl as described above.

Reaction temperature: 250°–275°C; reaction pressure: 20 atm.

Recycle of end gas: was employed but no specific statement was given of the recycle ratio of end gas to fresh feed gas.

Space velocity: of fresh feed gas was about 80 volumes per volume of slurry per hour at 250°C and 125 at 275°C.

Number of stages: only one stage was operated. For a full-scale plant three stages are recommended by Michael with condensation of oil and removal of carbon dioxide from the off gases from each stage.

Space-time-yield: was 10 kg of gasol ($C_3 + C_4$) plus oil per cu m of slurry per hr for single pass in the 1.5-cu-m reactor at 250°C and at a space velocity per hr of 80. At 275°C and a space velocity per hr of 125 the space-time-yield was 15 kg of gasol plus oil per cu m of slurry per hr.

Conversion: was about 70 per cent of the entering CO in single-stage 1.5-cu-m reactor.

Specific yield: of reaction products, in grams per cubic meter of H_2 + CO reacted, was as follows:

CO_2	H_2O	$CH_4 + C_2H_6$	$C_3 + C_4$	Oil, Boiling Range, °C			Water-Soluble Organic Material
				To 200	200–350	Above 350	
47.5	44	10	18	77	47	31	9

These figures show 173 g of gasol plus oil per cu m of H_2 + CO reacted. Assuming 95 per cent conversion in multistage operation, the specific yield of gasol plus oil would be 164 g per cu m of fresh feed gas, and the space-time-yield at 80 space velocity would be 13 kg per cu m of slurry per hr.

Typical gas analyses of fresh feed and end gas (from single-stage operation, volume per cent):

	CO_2	C_nH_m	H_2	CO	C_nH_{2n+2}	n in C_nH_{2n+2}	N_2
Fresh feed gas	0.8	0.0	40.8	53	2.0	1.8	2.8
End gas	30.4	3.0	28.4	27.8	4.0	1.5	6.4

These data show a contraction of 56.3 per cent, and a H_2:CO usage ratio of 0.69. This ratio indicates that there was little, if any, recirculation of end gas.

Analysis of oil product: is shown in Table 56. Olefins were determined by hydrogenation.

Table 56. Analysis of Oil Product of I.G. Farben. Slurry; Operation at 250°C, 20 atm of $0.8H_2$:1CO

(All per cents are by weight.)

Boiling Range, °C, of Fraction	Per Cent of Total Oil	Per Cent of Fraction			
		Alcohols	Olefins	Paraffins	Esters and Acids
To 50	4	0	85	12	3
50–100	20	5	83	7	5
100–150	16	15	67	11	7
150–200	10	12	62	20	6
200–250	12	12	63	17	8
250–300	10	10	54	25	11
300–350	8	5	45	38	12
Above 350	20	..	..	..	..

According to Michael [92] a good motor gasoline can be produced by the slurry process operating at 275°–290°C, and a high-grade Diesel oil by operation at lower temperatures (240°–260°C). The crude, 200°C-end-point gasoline had a motor octane rating of 60, and the refined gasoline

[92] T.O.M. Reel 166, Frames 795–7.

had a motor octane rating of 68. The Diesel oil boiling in the range 200°–300°C had a cetene number of 60, and a pour point of minus 10°C.

Further development of the slurry process was undertaken in 1946 by the Bureau of Mines, U. S. Department of Interior. Some physical

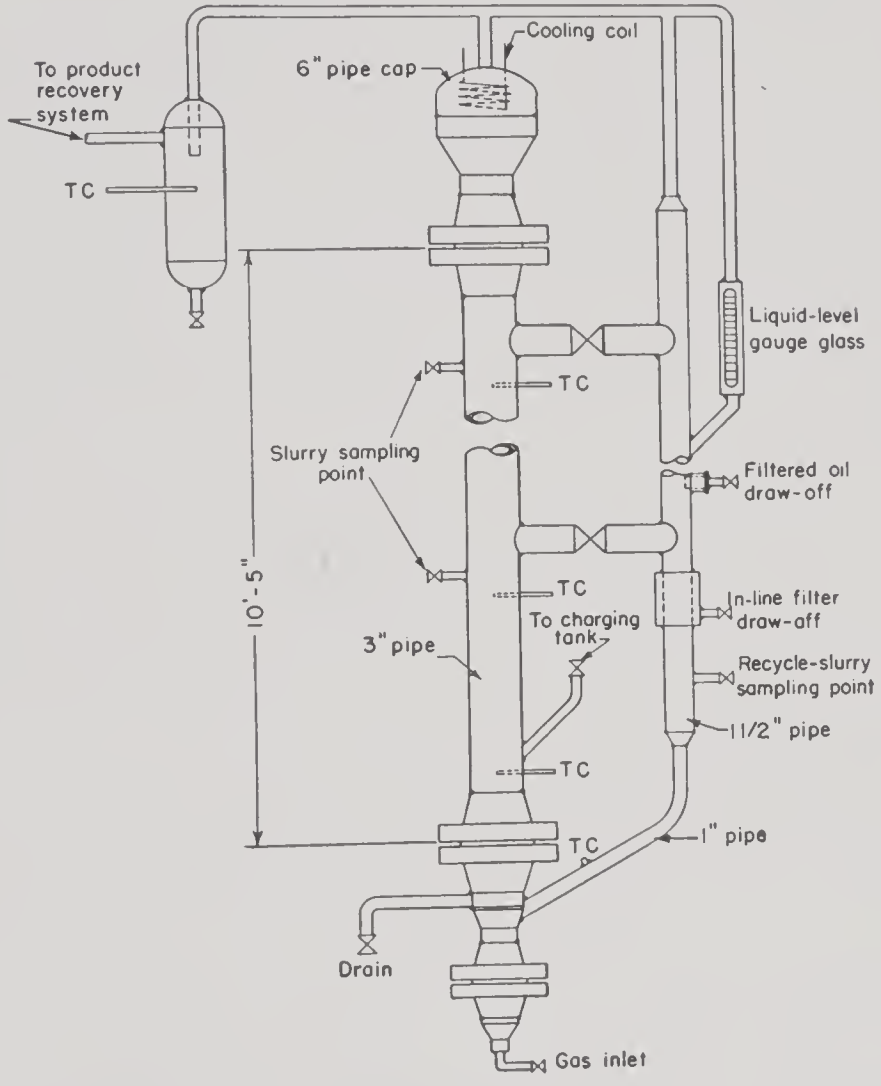


FIGURE 4–20. Liquid-phase catalyst suspension unit.

measurements were made in laboratory equipment to determine the gas velocities necessary to keep different concentrations of catalyst in the slurry in uniform suspension. A small pilot plant was then built and operated. Its design is shown in Figure 20. A slurry depth of 10 ft was provided in a 3-in.-diameter cylindrical reactor. Gas-lift circulation was maintained through a cross-over valve at either the 5-ft or 10-ft level to a 1.5-in. recycle leg. Slurry re-entered the reactor at a point below the 3-in. section and above the gas-inlet port. Preliminary tests showed no advantage in the use of porous plates for gas distribution; and, there-

fore, the gas inlet was a $\frac{1}{4}$-in. pipe connected to a conical reducer attached to the 3-in. reactor.

The liquid level in the reactor was observed in a gauge glass at the 10-ft level and controlled by withdrawing oil through one or both of the filters in the recycle leg. Above the 3-in. section the reactor was widened to 6 in. to provide additional volume in case of liquid surges and to reduce the linear velocity so as to effect adequate separation of gas from the slurry. A cooling coil was placed in the top of the 6-in. section to provide reflux to the top of the reactor.

Runs of 500–1,250 hr have been made to study the important process variables. No durability tests have yet been done. A precipitated 100Fe:5Cu:0.5K_2O catalyst was dried, suspended in a Fischer-Tropsch Diesel oil fraction boiling from 300° to 350°C, and ground in a ball mill. An initial slurry concentration of 36.6 weight per cent of catalyst was obtained; this was equivalent to an iron concentration of 21.5 weight per cent. The catalyst was inducted by passage stream of $1H_2 + 1CO$ gas through the slurry while gradually increasing the temperature and pressure. The operating temperature was in the range 240°–275°C and the pressure was 250 psi of $1H_2 + 1CO$ gas. Typical results of single pass operations with no end-gas recycle and with about 70 per cent CO conversion per pass are as follows:

Specific yield: 100–125 g of gasol plus oil per cu m of feed gas, containing less than 0.5 per cent of inerts.

Product distribution: in per cent of CO reacted:

CO_2	$C_1 + C_2$	$C_3 + C_4$	C_5+	Water-Soluble Material
45	6	7	37	5

The C_5+ boiling range, volume per cent, was about: to 200°C, 48; 200°–325°C, 15; above 325°C, 27.

Use ratio, H_2:CO: in the range 0.6–0.75.

Space velocity: 300 volumes of $1H_2 + 1CO$ per volume of slurry per hr.

Space-time-yield: of gasol plus oil was about 17 kg per cu m of slurry per hr.

GAS-PHASE SUSPENSIONS

The application of fluidized-catalyst techniques developed in the petroleum industry for catalytic cracking of oil vapors to the Fischer-Tropsch synthesis was effected by several American oil companies during

the past few years.[93–112] Most of the pilot-plant development work on the fluidized-iron-catalyst process has been done in reactors 2–8 in. in diameter and 10–24 ft high. Temperature is controlled by internal heat exchangers (cooling bayonets) hung in the top section of the reactor, or by a cooling jacket surrounding the reactor. In an 8-in. jacketed reactor the vertical temperature gradient in the catalyst bed is about 25°F. The operating temperature and pressure ranges are 585°–650°F and 400–650 psi, respectively. Cheap natural gas is the proposed raw material for the process, and therefore most of the experimental and pilot-plant development work was done with $1.8–2H_2 + 1CO$ gas which can be obtained directly by reaction of natural gas with steam and oxygen. Recycling of about 2 volumes of end gas per volume of fresh gas was practised in all the experimental work. In the early stages of this work commercially available synthetic-ammonia catalyst containing about 97 per cent Fe_3O_4, 2.5 per cent Al_2O_3, 0.5 per cent K_2O was used. More recently cheaper, although equally active, catalysts prepared by addition of 0.5 per cent K_2O to naturally occurring magnetite or to steel mill scale have been used. The catalyst is ground to particles 2–100 microns in diameter and completely reduced in a fluidized bed with dry hydrogen at 350°–460°C. After reduction, the temperature is lowered to about 290°–300°C, increasing amounts of synthesis gas are gradually introduced, and the pressure is slowly increased over a period of several days. After this preliminary treatment operation proceeds at a linear gas velocity of about 0.7 ft per sec. The operation usually is of the

[93] E. V. Murphree, C. W. Tyson, D. H. Campbell, and H. Z. Martin, U. S. Patent 2,360,787 (1944).
[94] J. E. Latta and S. W. Walker, *Chem. Eng. Progress*, **44**, 173–6 (1948).
[95] P. Ryan, *Oil Gas J.*, **43**, No. 47, 264 (1945).
[96] P. C. Keith, *Oil Gas J.*, **45**, No. 6, 102 (1946).
[97] E. A. Johnson, U. S. Patent 2,393,909 (1946).
[98] G. Roberts, Jr., and J. A. Phinney, *Oil Gas J.*, **45**, 72–3, 139–41 (1947).
[99] H. V. Atwell, U. S. Patent 2,452,712, Nov. 2, 1948.
[100] S. B. Sweetser, U. S. Patent 2,453,874, Nov. 16, 1948.
[101] W. G. Scharmann, U. S. Patent 2,451,879, Oct. 19, 1948.
[102] L. C. Rubin, U. S. Patent 2,448,279, Aug. 31, 1948.
[103] H. J. Ogorzaly, U. S. Patent 2,458,870, Jan. 11, 1949.
[104] T. C. Main, U. S. Patent 2,459,444, Jan. 18, 1949.
[105] J. K. Roberts, U. S. Patent 2,461,570, Feb. 15, 1949.
[106] C. E. Hemminger, U. S. Patent 2,464,505, Mar. 15, 1949.
[107] W. G. Scharmann, U. S. Patent 2,463,912, Mar. 8, 1949.
[108] S. D. Sumerford, U. S. Patent 2,471,913, May 31, 1949.
[109] P. C. White, U. S. Patent 2,476,788, July 19, 1949.
[110] M. A. Segura, U. S. Patents 2,476,920, July 19, 1949; 2,479,420, Aug. 16, 1949.
[111] N. L. Dickinson, U. S. Patent 2,481,089, Sept. 6, 1949.
[112] S. W. Walker, U. S. Patent 2,485,945, Oct. 25, 1949.

"fixed" fluidized-bed type, *ie*, with very little "carry over" of catalyst in the off gas. Conversion usually is of the order of 90 per cent, specific yield is about 150 g of C_3+ per cu m of fresh gas, and space-time-yield is about 180 kg per cu m of fluidized catalyst volume per hr. This space-time-yield is 10–20 times that of the Ruhrchemie process and results in a great simplification and reduction in costs of reactor fabrication and installation. All the heat of reaction is converted to steam at 300–400 psi in the internal heat exchanger. The product is chiefly a good motor gasoline; an important secondary product is water-soluble organic material (chiefly ethanol and acetic acid, with smaller amounts of acetone, acetaldehyde, and higher alcohols). This process is estimated to produce motor gasoline at a somewhat lower cost than that of gasoline produced by existing petroleum conversion and refining procedures.

Severe operating difficulties were encountered in the pilot-plant development because of carbon formation. Main [104] of the Standard Oil Development Company states:

> It is known that particles of highly active and selective hydrocarbon-synthesis iron catalysts break down very rapidly under synthesis conditions to very much smaller particle diameter. The mass of iron powder which once possessed good fluidization properties becomes difficultly fluidizable and the hydrocarbon-synthesis operation must be discontinued. The breakdown of iron particles is probably caused by reaction of iron with carbon monoxide feed. The fluffy nature of this mass makes fluidization difficult if not impossible.

Main proposes to extend the useful life of a fluidized iron catalyst by the addition of sufficient inert solids such as sand, dolomite, alumina, or silica gel of such particle size as to maintain constant the essential fluidization characteristics of the catalyst bed. This procedure presents the severe difficulty of avoiding classification in the fluidized bed, and at best is a palliative and not a solution of the basic problem of carbon formation. Ogorzaly [103] and Scharmann [101] propose that the catalyst be circulated from the reactor to a "stripping" vessel where treatment with hydrogen or synthesis gas at lower pressures and higher temperatures would remove high-boiling organic material from the catalyst and thus increase its useful life. Scharmann [107] of the Standard Oil Development Company describes the difficulties encountered in the fluidized iron process as follows: "More particularly, carbon or coke deposits have been found to cause rapid disintegration of the catalyst particles leading to a substantial and undesirable expansion of the fluidized bed and ultimately to the requirement of complete catalyst-replacement because of fluidization difficulties." Scharmann [107] argues that because, in the fluidized iron process, as high as 70–80 per cent conversion in a single pass is obtained even at very high space velocities,

only a small fraction of the catalyst bed accomplishes most of the synthesis, and consequently at normal space velocities the catalyst grains first encountered by the synthesis gas are overheated. The implication of his argument is that despite overall efficient heat transfer the "skin temperature" of the catalyst grains is much higher than the average reactor temperature, and that this condition is largely responsible for rapid carbon deposition. He proposes a two- or three-stage fluidized iron process in which only 20–50 per cent of the total conversion will be achieved in the first stages, using a low catalyst bed density of 2–15 lb per cu ft. The remaining $H_2 + CO$ is to be converted in the last stage, using a denser catalyst bed of 25–100 lb per cu ft.

To illustrate the advantages of his proposed process Scharmann [107] states:

> At the conditions set forth in the preceding description of my invention, the hydrocarbon synthesis on catalysts of high activity and selectivity to liquid products but normally strong carbonization tendency such as, for example, an iron catalyst obtained by a suitable reduction of a composite containing about 95.4 parts by weight of Fe_2O_3, 2.6 parts by weight of Al_2O_3, and 2.0 parts by weight of K_2O * and 1.4 parts by weight of SiO_2,† may be operated in a fully continuous manner at constant operating conditions for several hundred hours with high liquid yields approaching or exceeding 200 cc of C_4+ hydrocarbons per cu m of $CO + H_2$ converted, without appreciable catalyst carbonization and disintegration which would result in catalyst bed expansion, catalyst losses, and difficulties in process control. On the other hand, when using the same catalyst in conventional fluid dense phase operation at otherwise comparable reaction conditions to obtain similar yields, changes observed after 100 hr of operation include the following: The carbon content has risen from close to zero to over 30 per cent by weight of iron, which is equivalent to about 0.8 to 1.0 per cent of the CO reacted. The proportion of catalyst fines of 0 to 20 microns size has increased by about 350 per cent resulting in an increase of catalyst bed volume by about 250 per cent and a decrease of catalyst bed density from about 55 lb per cu ft to about 14 lb per cu ft. These changes necessitate a rapid catalyst replacement and a current readjustment of operating conditions.

That Scharmann's analysis [107] of the temperature gradients from the surface of the catalyst grains to the gas phase probably is correct is indicated by the disclosures of Hemminger.[106] The latter states that the amount of carbon deposition per unit of oil synthesized decreases rapidly with increasing space velocity of the reaction gas. He proposes to use very high linear velocities, and to carry over and recirculate 500–2,000 lb of catalyst per 1,000 cu ft of feed gas. To decrease carbon formation

* The alkali content of this catalyst is too high and probably was partially responsible for the rapid carbon deposition.

† Apparently an error exists, for the composition of the catalyst as given adds up to 101.4 per cent.

further, he suggests operation with a relatively low temperature of 550°F in the bottom of the reactor and 700°–750°C at the top.

Roberts [105] also proposes what is essentially a two-stage operation for the fluidized iron process, plus the added disclosure that to minimize carbon deposition it is necessary to operate with a relatively high partial pressure of hydrogen in the total feed gas (fresh gas plus recycle end gas). He states:

> With iron catalyst . . . there is a serious tendency towards catalyst defluidization after a very short time on stream. It has been found that by diluting the synthesis gas charge with a gas rich in carbon dioxide and/or hydrogen so that the H_2:CO:CO_2 ratio is approximately 3:1:2 or within the range 2–6:1:1–3 and the carbon monoxide content is kept below about 15 per cent and preferably of the order of about 10 to 12 per cent by volume, the tendency toward defluidization is minimized and the reaction is directed toward the production of desired products. However, a freshly prepared or freshly reactivated iron catalyst which is highly active cannot be placed on stream with the optimum gas charge under the desired conversion conditions because the catalyst will tend to "wax up" (become coated with carbonaceous matter), agglomerate and/or defluidize. It has heretofore been necessary to employ a long start-up procedure for conditioning the catalyst, using a gas charge initially almost free of carbon monoxide and gradually increasing the carbon monoxide content while temperatures and pressures are likewise increased and brought up to conversion conditions. This procedure of conditioning a fresh active catalyst has been highly disadvantageous in that it has required days and weeks of time during which the system does not function at designed capacity.
>
> In accordance with my invention I employ at least two separate reactors and I condition freshly prepared or activated catalyst in one of these reactors with residual gas from the product recovery system. I may employ the off gases from this conditioning reactor as a diluent for the incoming synthesis gas stream for regulating the H_2:CO:CO_2 ratio. Thus, when the properly diluted charge passes through the main on-stream reactor under conversion conditions, assuming that the catalyst in said reactor has been properly conditioned, substantially complete conversion of carbon monoxide is effected and the residual gas from the product recovery system, after removal of water, will be fairly rich in hydrogen but will contain only about 1 per cent of carbon monoxide. A portion of this residual gas stream is ideal for conditioning freshly prepared or reactivated catalyst. The conditioning is accomplished in the other reaction chamber and the off gases from said other reaction chamber may form the diluent for the externally introduced synthesis gas stream.
>
> There is a tendency for the activity of the synthesis catalyst to decrease with time on stream, so that the residual gas from the product recovery system will at first be substantially free from carbon monoxide and then will gradually contain more and more carbon monoxide. By employing this residual gas for conditioning active catalyst, the highly active catalyst is first treated with a gas of very low carbon monoxide content and it is thus rendered capable of handling more and more carbon monoxide as the carbon monoxide content of the residual gas increases. By the time the main synthesis catalyst requires reactivation, the

conditioned catalyst is ready for use in the main synthesis step so that the process may be carried out continuously with a substantially constant load on the various parts of the system.

Roberts [105] prefers to start with a H_2:CO ratio of 2 in the fresh feed, and cites as catalysts the following:

1. Fused magnetite (obtained by burning pure iron in a stream of oxygen) promoted with small amounts of one or more of substances such as silica, alumina, titania, or alkali metal oxide. These are similar and in some cases identical with commercially used synthetic-ammonia catalysts.
2. Hematite (Fe_2O_3) mixed with about 2 per cent of potassium carbonate, and the mixture sintered at 1,832°F. This converts the Fe_2O_3 to Fe_3O_4. Then the excess potassium is extracted with water so that only about 0.5 per cent of potassium remains, and the catalyst is dried and reduced with hydrogen for several hours at 600°–1,200°F.

Roberts [105] states:

> Either after or before reduction the particles should be ground to desired particle size and when the catalyst is reduced after grinding, it may be desirable to subject the catalyst to a sintering step in a hydrogen atmosphere at a temperature of 1,100° to 1,300°F. It appears that the active catalyst is a mixture of Fe and FeO and that in the conditioning step a portion thereof is converted to Fe_2C.
>
> When the catalyst is used in a fluidized solids system its particle size . . . should preferably be in the range 2 to 100 microns. For optimum results the particles should be of indiscriminate or different sizes rather than uniformly sized. The bulk density of the compact catalyst particles may be from 100 to 150 lb per cu ft but when fluidized by the upward passage of gases at the rate of 0.5 to 3 ft per sec preferably 1 to 2 ft per sec, the fluidized density is below 90 lb per cu ft and may range from 25 to 75, or of the order of about 50 lb per cu ft.

It may be inferred from Roberts' [105] disclosure that a critical partial pressure of hydrogen exists below which the process is not operable without continuous changes in operating controls. Possibly it would be more satisfactory to state this critical partial pressure in pounds per square inch in the off gas at reaction temperature. For Roberts' [105] conditions this would be of the order of 100–150 lb per sq in. Further detailed experiments and pilot-plant operation seem essential to determine this limiting partial pressure and to ascertain the advantages and disadvantages of exceeding it.

Roberts [105] describes a full-scale reactor as a cylindrical vessel 25 ft in diameter and about 45 ft high, containing about 120 tons of iron catalyst. At a catalyst bed density of 50 lb per cu ft, 120 tons would occupy a volume of 4,800 cu ft, and therefore less than one-fourth of the total re-

actor volume (21,000 cu ft) was occupied by catalyst. Internal cooling bayonets are suggested to remove heat of reaction. The operating temperature and pressure ranges specified are 550°–700°F and 150–450 psi, respectively. Composition of the total feed gas (fresh gas H_2:CO = 2 plus recycle end gas with H_2:CO ratio about 10) is given as 34 per cent H_2, 12 per cent CO, 24 per cent CO_2, 30 per cent CH_4 plus higher hydrocarbons. The volume of fresh feed gas is 135 million cu ft per day and of total feed 400 million cu ft per day. The volume of carbon monoxide fed per hr per lb of iron in the catalyst charge is about 12 cu ft; the volume of total feed per cu ft of catalyst per hr is about 3,500 cu ft; and the space velocity of fresh feed based on the catalyst volume is about 1,200 per hr. Assuming that Roberts [105] obtained about the same yield as indicated by Scharmann,[107] *ie*, 200 cc of C_4+ per cu m of gas converted, a specific gravity of 0.7, and 93 per cent conversion, calculation indicates a specific yield of 130 g of C_4+ per cu m of fresh feed gas and a space-time-yield of 156 kg of C_4+ per cu m of fluidized catalyst volume per hr. Assuming that the C_3+ yield is 15 per cent of the C_4+, the specific yield of C_3+ is about 150 g per cu m of fresh feed gas and the space-time-yield is about 180 kg per cu m of fluidized catalyst volume per hr.

It is apparent from Roberts' [105] disclosure that he is providing for a large increase (about 300 per cent) in catalyst bed volume during the useful life of the catalyst. If relatively cheap catalysts are used and their useful life is limited to about 500 hr, after which they could be discarded, it probably will not be necessary to use a total reactor volume of more than 2 times the initial volume of fluidized catalyst. This would decrease Roberts' [105] reactor volume to about 10,000 cu ft. It may be assumed as a first approximation that about 2,500 cu ft of this space is essential for cooling bayonets and headers, and that the remaining excess (above the 4,800 cu ft occupied initially by the fluidized catalyst) of about 2,700 cu ft is for expansion of the bed and for disengagement of catalyst from reactor gas. To compare the space-time-yield of the fluidized iron process with that of other processes, this yield should be calculated on the basis of 4,800 + 2,700 = 7,500 cu ft of catalyst volume. On this basis the space-time-yield of C_3+ is 115 kg per cu m of catalyst volume per hr. Although this is about twice the space-time-yield of the oil-circulation process, the specific yield of about 150 g of C_3+ per cu m of inert-free fresh gas of the fluidized iron process is lower than that of the other process. The oil-circulation process is expected to yield 165–170 g of C_3+ per cu m of inert-free fresh gas. When coal is the raw material, the cost of synthesis gas preparation will be about 60 per cent of the total cost of the liquid fuel product, and an increase

of 10–15 per cent in specific yield will be a difficult handicap for the fluidized process to overcome despite its larger space-time-yield.

The results of some of the recent pilot-plant experiments done in the Stanolind Oil and Gas Company at Tulsa, Okla., are given in a patent by S. W. Walker.[112] The catalyst was prepared from steel mill scale, which was ground to give the following screen analysis in weight per cent:

On 100 mesh	23
100–140 mesh	32.8
140–200 mesh	19.8
200–325 mesh	19.8
Through 325 mesh	4.6

The powdered scale was impregnated with 0.5–2.0 per cent of K_2O, using an aqueous solution of potassium carbonate or nitrate. The alkali-impregnated mill scale was reduced in the fluidized state at 700°–775°F with hydrogen at 50 psi for about 70 hr. The reduced catalyst contained 95.5 per cent of elemental iron and 97.1 per cent of total iron. Experiments were conducted in water-jacketed cylindrical reactors of two sizes: 2 in. by 20 ft and 8 in. by 30 ft. The catalyst charge to the 2-in. reactor was 15 lb and that to the 8-in. reactor was 214 lb. Initial density of the fluidized bed was 100 lb per cu ft, and after 400 hr of operation the density was 30 lb per cu ft. In the top of the reactors stone filters were inserted to separate catalyst dust suspended in the product gases. About 5 per cent of the carbon monoxide in the feed was reacted on the powdered catalysts adhering to the stone filters. Data presented [112] on the effect of catalyst age and reaction temperature on the product distribution are reproduced in Table 57. All other operating variables were held constant as follows:

Linear velocity	0.6–0.65 ft per sec
Pressure	250 psi
Recycle ratio of end gas to fresh gas	1.7:1
H_2:CO ratio in fresh gas	2.6:1
Analysis of total feed, volume per cent	$30H_2$, 10CO, $17CO_2$, $23N_2$, $20CH_4$ and higher hydrocarbons

The large variations in rate of catalyst density decline of Table 57 are probably not as significant as the statement that during 400 hr of operation the density decreases from 100 to 30 lb per cu ft. The effects of changing reaction temperature in the range 600°–660°F are small and obscured by changes in catalyst activity. The data show a maximum of about 90 per cent conversion of carbon monoxide, and an average of 8.0 per cent of the reacted carbon monoxide going to produce CO_2, 26

TABLE 57. STANOLIND PILOT-PLANT DATA FOR FLUIDIZED IRON PROCESS

Catalyst age, hr	20	68	92	116	140	164	235	259	283	355	404	477	499
Average temperature, °F	600	600	600	620		640		660		600		580	
Per cent conversion of CO in feed	86.3	81.2	81.5	84.0	82.1	81.1	78.4	80.0	78.9	85.3	86.6	89.0	87.2
Per cent C to													
CO_2	5.9	4.2	5.2	7.0	7.8	7.9	9.3	7.3	9.2	11.7	9.3	8.9	10.6
$C_1 + C_2$	26.4	24.6	31.5	31.4	27.6	26.1	27.7	39.4	26.3	22.1	21.3	20.0	19.8
$C_3= + C_4=$	21.4	16.9	20.4	18.8	19.9	19.8	20.8	13.4	18.0	20.1	21.4	22.6	21.4
$C_3 + C_4$	4.1	5.9	5.4	4.9	5.6	5.7	3.5	2.9	3.2	3.5	4.5	3.6	4.3
C_5+	35.5	41.5	32.0	31.1	32.2	33.3	31.2	29.4	34.8	31.4	32.8	32.4	31.8
Oxygenated compounds	6.6	6.8	5.6	6.7	6.9	7.2	7.5	7.7	8.5	11.2	10.2	12.6	12.1
Rate of density decline, lb per cu ft per hr		0.04		0.28		0.0		0.0		0.07		...	
Carbon deposition, lb per 100Fe per hr		0.03		0.09		0.05		0.01		0.03		...	
Increase in minus 325 mesh, lb per hr		0.12		0.08		0.36		0.08		0.05		...	

per cent to $C_1 + C_2$, 19.6 per cent to $C_3= + C_4=$, 4.4 per cent to $C_3 + C_4$, 33 per cent to C_5 and higher hydrocarbons, and 8.4 per cent to oxygenated organic compounds.

Based on the pilot-plant tests described above, a commercial-size plant (about 8,000 barrels per day) was designed [94, 96, 98] and is being erected at Brownsville, Texas. Synthesis gas is to be made by reacting natural gas at 400–500 psi with oxygen and steam in two refractory-lined vessels each about 2,000 cu ft in volume. The synthesis converters for the Brownsville plant are stated to be six in number, and each of about 3,500-cu-ft volume. The total reactor volume of 21,000 cu ft for 8,000 barrels of oil per day corresponds to a space-time-yield of

Table 58. Proximate Product Distribution of Hydrocol Process

	Weight Per Cent of Total	Olefin Content, volume per cent
$C_3 + C_4$	32	80
Naphtha	56	70
Diesel	8	65
Residue	4	..

Table 59. Isomeric Composition of Hydrocol Product C_3, C_4, and C_5 Fractions

(Per cent by weight)

Component	C_3 Fraction	C_3–C_4 Fraction
Propane	20.2	11.6
Propene	79.8	45.7
	C_4 Fraction	
n-Butane	13.6	5.8
i-Butane	1.9	0.8
Butene-1	64.3	27.5
Isobutene	8.7	3.7
Butene-2	11.5	4.9
Total unsaturates	84.5	81.9
	C_5 Fraction	
n-Pentane	7.9	
Isopentane	3.5	
Pentene-1	67.2	
Pentene-2	5.8	
2-Methylbutene-1	3.5	
3-Methylbutene-1	11.1	
2-Methylbutene-2	0.7	
Cyclopentane	0.1	
Cyclopentene	0.2	
Total unsaturates	88.5	

about 80 kg per cu m of total reactor volume per hr; so that in this design the fluidized-catalyst volume is about $\frac{8.0}{18.0} = 0.445$ of the total reactor volume. In a design for a similar plant in the Hugoton (Kansas) natural gas field only two reactors were specified.[94] Internal heat exchangers will be suspended in the top section of the reactors in the Brownsville plant.

Some information is available [113] concerning the quality and isomeric composition of the gasoline produced by the fluidized-iron-catalyst process (commercially known as the Hydrocol process). The data of Tables 58, 59, 60, and 61 contain analyses of products from The Texas Company pilot plants at Beacon, N. Y., and Montebello, Calif.

Table 60. Fractionation of Hydrocol Naphtha, Distillation at 20:1 Reflux Ratio in 6 ft by $\frac{1}{2}$ in. Podbielniak Column

Assumed Carbon Number	Cut Point, °C	Volume Per Cent of Naphtha	Olefin, Weight Per Cent of Fraction [a]
6	75	20.4	85.2
7	105	23.4	89.2
8	130	18.7	89.8
9	155	14.2	88.3
10	175	10.7	90.3
11	195	7.6	90.7
Residue		5.0	....

[a] The olefin content was calculated from the bromine number on the assumption of mono-olefins of the carbon number given in the first column. Because of the presence of oxygenated organic compounds in the naphtha fractions the olefin percentages probably are too high. The error may be as great as one-third of the figure reported.

Table 61 shows that only a very small amount of dimethyl isomers is present. These data combined with similar data for the product from cobalt catalysts (see p 363, this chapter) indicate that a basic character-

Table 61. Mass Spectrometric Determination of Isomeric Composition of Hydrogenated Hydrocol C_6, C_7, and C_8 Fractions

(Figures are in weight per cent of each fraction.)

Constituent	C_6	C_7	C_8
Normal hydrocarbons	75.9	60.2	55.4
Monomethyl isomers	20.0	29.3	36.6
Dimethyl isomers	0.4	1.7	2.4
Cyclic isomers	3.7	8.8	5.6

[113] F. H. Bruner, The Composition and Quality of Synthetic Gasoline from Natural Gas, *Ind. Eng. Chem.*, **41**, 2,511 (1949).

istic of the Fischer-Tropsch process is the high ratio of mono- to dimethyl isomers in the product. Ultraviolet absorption spectra of the C_6 and C_7 unhydrogenated fractions showed about 2 per cent benzene in the former and 5 per cent toluene in the latter.

The C_3–C_4 fraction, of composition shown in Table 58, is readily polymerized, using Universal Oil Products Company phosphoric acid-P_2O_5 polymerization catalyst at 400°F, 500 psi, 1.15 volumes of liquid feed per volume of catalyst per hour. The conversion was over 90 per cent of the olefin charged, and 88 per cent of the polymer boiled below 400°F. The 400°F-end-point polymer had a motor octane number of 82.4, and this increased to 85.9 upon the addition of 3 cc of tetraethyllead per gal.

The 400°F-end-point Hydrocol naphtha fraction had a motor octane number of 62. Upon catalytic refining (probably over bauxite at 700°–800°F) the motor octane number increased to 75.9. After addition of 1 cc of tetraethyllead per gal of treated naphtha, the motor octane number increased to 80.5 and after addition of 3 cc it increased to 82.1. The total Hydrocol gasoline product would consist of 25 per cent C_3–C_4 polymer, 11 per cent *n*-butane, and 64 per cent treated naphtha. This gasoline would have an API gravity of 65.8 and Reid vapor pressure of 9.2 lb; it would have a clear motor octane number of 80.2 and, with 3 cc of tetraethyllead per gal, a motor octane number of 84.1.

Weitkamp [114] made a careful study of the products from a fluidized-iron-catalyst operation in the Stanolind Oil and Gas Company's pilot-plants. His results on the isomeric composition of the hydrogenated C_4, C_6, and C_7 fractions are given in Table 62. The results are in excellent agreement with those of Bruner.[113] Weitkamp searched care-

Table 62. Isomeric Composition of Hydrogenated C_4, C_6, and C_7 Fractions of Product from Fluidized Iron Catalysts

(Per cent by weight.)

Component	Per Cent	Component	Per Cent
n-Butane	89.5	*n*-Heptane	63.2
i-Butane	10.5	2-Methylhexane 2,3-Dimethylpentane	10.2
n-Hexane	73.1	3-Methylhexane	15.5
2-Methylpentane	12.3	2,4-Dimethylpentane	0.9
3-Methylpentane	11.1	Naphthenes	5.1
2,3-Dimethylbutane	2.1	Aromatics	5.1
Naphthenes	1.3		
Aromatics	0.5		

[114] A. W. Weitkamp, *The Composition of Hyrocarbon Synthesis Product*, presented at Gordon Chemical Research Conference, Catalysis Group, New London, N. H., June 22, 1949.

fully for even traces of compounds with quaternary carbon atoms but did not find any. Weitkamp's fractions C_4–C_7 contained 75–90 per cent of olefins. Thus the C_6 fraction contained 87.5 per cent of olefins of the following types:

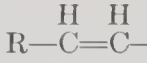
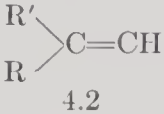
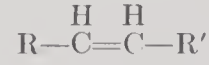
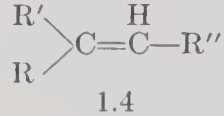
Type				
Per cent	79.6	4.2	1.0	1.4

Figure 21 shows the per cent of *n*-aliphatics, of branched aliphatics plus naphthenes, and of aromatics in the fractions C_1–C_{25}. The aro-

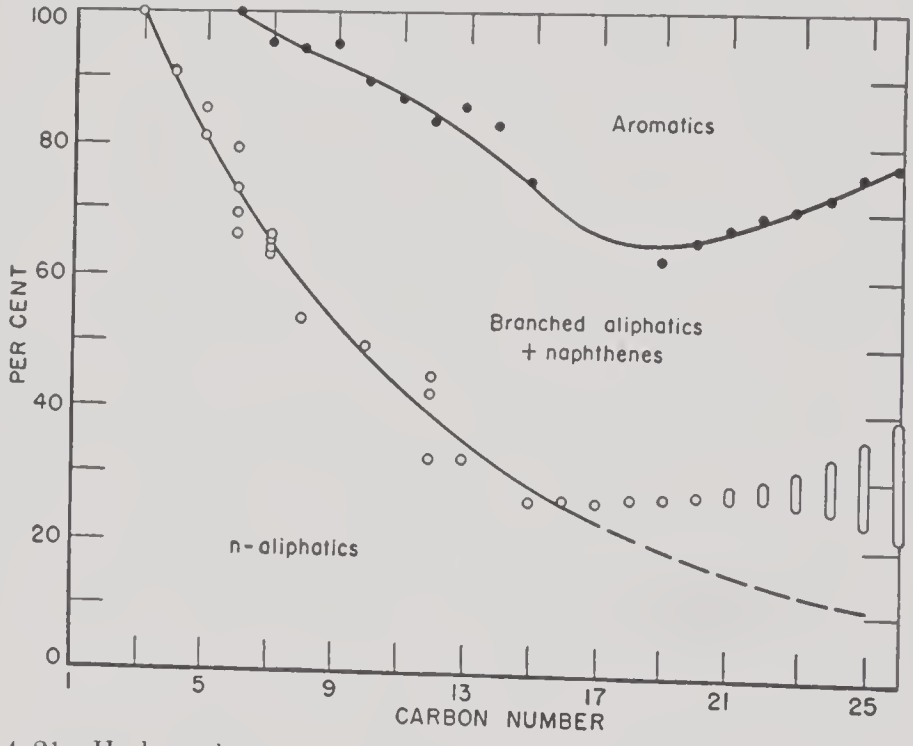


FIGURE 4–21. Hydrocarbon product distribution, fluidized iron process. Reproduced from reference 114.

matics were separated by silica gel adsorption, and the results are quite reproducible. Aromatics with more than one ethyl or larger alkyl group were sought but not found. The composition of the aromatics in the C_8 and C_9 fractions is given in Table 63. The separation of *n*-aliphatics from the branched aliphatics plus naphthenes depends upon the fact that urea forms a complex with straight-chain paraffins but does not form complexes with branched-chain paraffins and naphthenes. The method cannot be applied for C_6 or lower carbon number fractions. In the range C_6–C_{11} the method is not as accurate as in the C_{12}–C_{19} range. For fractions of carbon number greater than C_{19} some branched isomers also form complexes with urea. The presence of functional groups does not interfere with the separation. Thus, for example, straight-chain

alcohols will form a complex but branched-chain alcohols will not. One molecule of urea per methylene group is necessary, so that, *eg*, to separate 1 mole of cetane or hexadecane 14 moles of urea are required. The sample usually is dissolved in isopentane, and solid, finely powdered urea is added. The mixture is cooled during the addition of urea and is stirred for 1 hr, filtered, and washed with isopentane. The crystalline complex compound is decomposed with water.

Table 63. Composition of Aromatics in C_8 and C_9 Fractions of Product from Fluidized Iron Catalyst

Component	Weight Per Cent	Component	Weight Per Cent
Ethyl benzene	41	1-Methyl, 2-ethyl benzene	19
o-Xylene	31	1-Methyl, 3-ethyl benzene	23
m-Xylene	20	1-Methyl, 4-ethyl benzene	9
p-Xylene	8	1,2,3-Trimethyl benzene	1
	—	1,2,4-Trimethyl benzene	6
Total C_8	100	1,3,5-Trimethyl benzene	1
n-Propyl benzene	39		—
i-Propyl benzene	2	Total C_9	100

Eliot, Goddin, and Pace [115] published some data on the yield and composition of oxygenated organic compounds produced by the fluidized iron catalyst in pilot plants of the Stanolind Oil and Gas Company. The catalyst was prepared from mill scale, and the synthesis was conducted at 550°–650°F and at 400 psi. About 2.4 gal of a water solution containing 5–10 per cent of oxygenated organic compounds was produced per gal of oil. It was found possible to obtain by simple distillation a rich distillate containing non-acid chemicals, and a dilute distillation residue containing the acids and the bulk of the water. Separation of compounds in the distillate was difficult because of formation of constant-boiling mixtures of alcohol, water, and ketones. Solvent extraction and extractive distillation procedures were necessary.

Table 64 indicates that more than 50 per cent of the water-soluble oxygenated compounds is alcohol. Of the alcohols, ethyl alcohol occurs to the greatest extent; of the ketones, acetone; of the aldehydes, acetaldehyde; and of the acids, acetic acid. The ratio of normal to isopropyl alcohol is about 10. Weitkamp [114] found that all the ketones are methyl ketones, and that bifunctional compounds, such as aromatic alcohols and acids, and keto or aldehydro acids, are not present. Unsaturated alcohols, ketones, and acids were found.

[115] T. Q. Eliot, C. S. Goddin, Jr., and B. S. Pace, *Chem. Eng. Progress*, **45**, 532–6 (1949).

TABLE 64. WATER-SOLUBLE ORGANIC COMPOUNDS FROM FLUIDIZED IRON CATALYST IN A 10,000-BBL-PER-DAY PLANT

(Figures are in tens of thousands of pounds per year and weight per cent of total.)

Alcohols	10,000 lb per Year	Per Cent	Aldehydes	10,000 lb per Year	Per Cent	Ketones	10,000 lb per Year	Per Cent	Acids	10,000 lb per Year	Per Cent
Methanol	60	0.3									
Ethanol	8,030	36.9	Acet	1,310	6.0				Acetic	3,930	18.1
n-Propanol	1,890	8.7	Propion	488	2.2	Acetone	1,630	7.5	Propionic	1,030	4.7
i-Propanol	164	0.8				Methylethyl	471	2.2			
Butanols	871	4.0	Butyra	457	2.1	Methylpropyl	194	0.9	Butyric	733	3.4
Pentols and higher	270	1.2				Methylbutyl	53	0.2	Valeric and higher	168	0.8
Total	11,285	51.9	Total	2,255	10.3	Total	2,348	10.8	Total	5,861	27.0

Eliot, Goddin, and Pace [115] state that the yearly production of oil-soluble oxygenated organic compounds by a 10,000-bbl-per-day plant would be 2,710,000 lb of alcohols, 2,780,000 lb of aldehydes and ketones, and 2,740,000 lb of acids.

Rubin [102] of the M. W. Kellogg Company describes the application of fluidized-catalyst techniques to the Fischer-Tropsch synthesis on cobalt catalysts. As a support for fluidized cobalt catalyst, kieselguhr was found to be not as desirable as an acid-treated bentonite type of clay

TABLE 65. FLUIDIZED COBALT-MAGNESIA-SUPER-FILTROL-CATALYST OPERATION WITH $2H_2 + 1CO$ FEED GAS CONTAINING 14 PER CENT OF INERTS (8 PER CENT CH_4 + 6 PER CENT CO_2)

Hours on conditions	30
Operating conditions	
Average catalyst temperatures, °F	
8.5 ft above gas entry port	389
4.5 ft above gas entry port	406
2.5 ft above gas entry port	410
0.5 ft above gas entry port	414
Feed-gas temperature, °F	414
Pressure, lb per sq in. at outlet	25
Bed conditions	
Height, ft	7.3
Density, lb per cu ft	46
Velocity, ft per sec, at inlet	0.62
Cu ft of feed gas per hr per cu ft of catalyst bed	585
Per cent of CO converted	76.0
Per cent of CO converted to $CH_4 + C_2H_6$	21.7

such as Super Filtrol. A typical cobalt catalyst for fluidized operation was prepared in a manner essentially identical with that described in Chapter 3, p 152, for cobalt-kieselguhr catalysts. After reduction, the filter-cake granules were ground in an atmosphere of carbon dioxide so that about all the powder passed through a 40-mesh screen, and about 30 per cent of it passed through an 80-mesh screen. The composition of the particular catalyst used to obtain the results given in Table 65 was, in parts by weight, 100Co:15MgO:200 Super-Filtrol. The reactor was a jacketed 2-in. pipe, 13 ft high. Temperature was controlled by circulating water or Dowtherm at reaction temperature through the jacket. The reactor contained 9 lb of catalyst.

Relative Efficiencies and Operating Costs for Different Processes

COMPARISONS OF OPERABILITY, SPECIFIC YIELD, AND SPACE-TIME-YIELD

Important criteria for comparison of different processes for Fischer-Tropsch synthesis are operability, yield of industrially valuable products per unit volume of synthesis gas, and yield per hour per unit volume of reactor. Operability is difficult to define and measure on a pilot-plant scale. Its importance, however, cannot be overemphasized. The basic requirement for satisfactory operability is that a steady state be reached within a relatively short time after starting the plant or after introduction of fresh catalyst in an operating plant. This steady state should persist with little, if any, change in operating conditions and character of product for a long enough period of time to keep operating and maintenance costs sufficiently low to provide an economically feasible process. In much of the pilot-plant work done in Germany on the hot-gas-recycle, the powdered-catalyst oil-slurry, and the oil-circulation processes, a steady state was not reached and the operability of the processes was not demonstrated. Indeed, one very erroneous conclusion, based on non-steady-state operation, was drawn as to the apparent methane and ethane yield in the powdered-catalyst oil-slurry process. In the United States, the fluidized-iron-catalyst and the oil-circulation processes only recently reached satisfactory levels of operability.

The durability of the steady state in the Ruhrchemie process was 150–200 days. In the fluidized-iron-catalyst process it is about 20 days, whereas in the oil-circulation process it is between 100 and 200 days. The high space-time-yield of the fluidized-iron-catalyst process compensates for the relatively short life of the steady state. Thus the total

weight of oil synthesized per pound of catalyst during the life of the steady state is approximately the same for the fluidized-iron-catalyst and the oil-circulation processes.

In Table 66 are shown the salient features of several Fischer-Tropsch processes. Two of these—the powdered-catalyst oil-slurry and the

TABLE 66. CHARACTERISTICS OF VARIOUS FISCHER-TROPSCH PROCESSES

Catalyst	Temperature, °C	Pressure, atm	C_3+, g per cu m	C_3+,[a] kg per cu m per hr	Gasoline[b]	Diesel[b]	H.O. + Wax[b]	Water-Soluble Chemicals[b]	Steel,[c] tons per bbl per day	Motor Octane No.[d]	Cetane No.
Granular catalyst, externally cooled, no gas recycle											
Co	175–200	1	140	8	56	33	11	[e]	2.7	50	100
Co	175–200	10	150	10	35	35	30	[e]	2.4	25	100
Fe	200–225	10	125	10	32	18	35	15	2.5	..	..
Granular catalyst, externally cooled, gas recycle											
Co	190–224	10	160	13	50	22	22	6	1.9	..	..
Fe	230	20	145	14	19	19	56	6	2.1	..	..
Fe	275	20	145	14	68	19	8	5	2.2	..	..
Powdered catalyst, oil slurry, gas recycle											
Fe	250–275	20	170	20	25	30	51	4	1.2	..	..
Granular catalyst, internally cooled, gas recycle											
Fe	240–280	20	170	58	58	10	24	8	0.7	74	78
Granular catalyst, hot-gas recycle											
Fe	300–320	20	140	32	70	17	1	12	0.7	75	50
Fluidized catalyst, gas recycle											
Fe	300–320	20	150	115	73	7	3	17	0.6	76	...

[a] Kilogram of total product, excluding water, carbon dioxide, methane, ethane, and ethylene per volume of reactor per unit time.
[b] Weight per cent of oil plus water-soluble product.
[c] In converter and its accessories only.
[d] Bauxite treated, but no T.E.L. added.
[e] Very small, less than 1 per cent.

granular-catalyst hot-gas-recycle processes—have not been developed to an operable level. They are included to indicate the progress that has been made in process development. Such progress has been quite marked in increase of space-time-yield (kilogram of C_3+ per cubic meter of reaction space per hour) and concomitant simplification of reactor design. The increase in specific yield (gram of C_3+ per cubic meter of inert-free synthesis gas) has been less striking, as only one operable process—the granular-catalyst, internally cooled (by oil circulation) process—has exceeded the best specific yield of the Ruhrchemie cobalt-catalyst, end-gas-recycle process. The importance of a high specific yield when coal is used as raw material for synthesis gas production is shown by the estimate that 60–70 per cent of the total cost of the product is the cost of purified synthesis gas.

Table 66 shows also the wide range of product distribution which may be obtained, using iron catalysts and varying the operating temperature. Concomitant changes in catalyst preparation and induction also are involved, as has been discussed in preceding sections of this chapter. Heavy oil and wax when produced at relatively low temperature, *ie*, 240°–280°C, are low in cyclic hydrocarbons and can be readily converted to Diesel oil by mild thermal cracking. The octane ratings of gasolines from iron catalysts are increased by 6–10 numbers after passage of these gasolines over bauxite at 280°–300°C. The pour points of the Diesel oils produced directly in the Fischer-Tropsch synthesis are, with one exception, higher than 0°C. For the hot-gas-recycle process it is reported that the Diesel oil pour point is minus 25°C.

OPERATING COSTS

Cost estimates have been published by Murphree [116] on production of motor fuel from petroleum, using conventional refining procedures, and from natural gas and coal, using the fluidized iron Fischer-Tropsch process. In his published estimates Murphree [116] included 15 per cent per year of the investment for capital charges (5 per cent for amortization and 10 per cent for return on the investment). For construction of Table 67 these charges were estimated and separated from Murphree's total costs. In separating the capital charges, it was estimated that the 5 per cent depreciation and the 10 per cent return were based on 38, 72, and 100 per cent of the total investments for petroleum, natural gas, and coal, respectively. Capital charges for production of crude petroleum and natural gas are included in the prices charged the processing plants for those materials, whereas the capital charges for coal are not included.

[116] E. V. Murphree, *Oil Gas J.*, **46**, 66–70, 95–6 (1948).

The steel requirements listed in Table 67 include steel for all raw material production and transportation as well as for processing and transportation of products to a central market area. The Fischer-Tropsch process, using coal as raw material, requires the least steel, chiefly because of the low steel needs for mining the coal and for transportation of the product. Initial plant investment is \$8,200–\$8,500 per bbl per day for the synthetic processes and \$6,500 for production and refining

TABLE 67. ESTIMATE OF DIRECT COSTS FOR GASOLINE FROM PETROLEUM, NATURAL GAS, AND COAL

Raw material	Petroleum	Natural gas	Coal
Cost of raw material	\$2.78 per bbl [a]	10¢ per 1,000 cu ft [b]	\$3.20 per ton [c]
Process	Catalytic cracking	Fluidized iron Fischer-Tropsch	Fluidized iron Fischer-Tropsch
Plant location	Gulf Coast	Gulf Coast	Western Pennsylvania
Market location	East Coast	East Coast	Western Pennsylvania
Dollars per bbl per day [d]	6,500	8,200	8,500
Tons of steel per bbl per day	7.8	7.9	5.2
Gasoline			
Per cent of total oil product	87	90	89
Cost, cents per gal			
Raw material	7.1	2.4	3.9
Manufacturing	3.6	3.7	4.3
Product transport	1.0	1.0	...
Total direct costs	11.7	7.1	8.2
Depreciation, 5 per cent	0.8	1.9	2.8

[a] Price delivered to refinery.
[b] Price in field after gathering.
[c] Does not include capital charges on mining.
[d] Initial investment.

of petroleum. Murphree's [116] gasoline manufacturing cost for the Fischer-Tropsch process, using coal, appears to be 3–4 cents per gallon too low, according to an estimate made by Roberts and Schultz.[117]

Foreseeable improvements which will increase operability and decrease operating costs are the development, for the fluidized iron process, of catalyst which will not catalyze the reaction $2CO = CO_2 + C$ and which will not be appreciably oxidized during the steady-state life of the catalyst, and the development of a more active and mechanically stable catalyst for the oil-circulation process so as to reduce further the yields of $C_1 + C_2$. Reduced and nitrided magnetite appears to be a more suitable catalyst for the fluidized iron process. The preparation and testing of this catalyst are described in Chapter 6. Although too much $C_1 + C_2$ is produced when $1CO + 1H_2$ synthesis gas is fed to this catalyst, the use of $1.5CO + 1H_2$ yields not more $C_1 + C_2$ than is produced

[117] G. Roberts and P. N. Schultz, *ibid.*, **48**, No. 19, 116–25 (1949).

by the catalysts presently used in the fluidized process. The nitrided catalyst has not formed carbon or appreciable amounts of oxide during 6 months in laboratory tests with granular (6–10 mesh) beds. It has not yet been tested in the fluidized state. When powdered coal is gasified by use of oxygen and steam, adjustment of the feed to equal parts by weight of oxygen and coal with about 0.6 part of steam will result in about $1.5CO:1H_2$ in the synthesis gas.[118,119] Catalyst development work for the oil-circulation process has indicated that certain iron ores when crushed to the desired size (about 20 mesh), reduced, and then impregnated *in vacuo* with alcoholic potassium carbonate solution are more active than the fused catalysts and do not spall under reaction conditions. These improvements in catalysts for the fluidized and the oil-circulation processes probably will appreciably increase process operability and reduce operating costs by 0.5–1.0 cent per gal of gasoline.

Because the largest item in the direct cost of production of gasoline from coal by the Fischer-Tropsch process is the cost of synthesis gas, cheaper gasification and gas purification processes are being sought. In development work on coal gasification processes for synthesis gas production it is desirable to provide conditions under which all the sulfur of the coal appears as hydrogen sulfide rather than as organic sulfur compounds. Recent unpublished work in the synthetic liquid fuels research and development laboratories of the U. S. Bureau of Mines on a process for hydrogenation of powdered coal in the fluidized state at 500–1,000 psi and at 500°–600°C has disclosed an interesting way of obtaining a char containing no organic sulfur. This procedure yields about 25 per cent of an aromatic oil, 10–15 per cent of gaseous hydrocarbons, and 45–55 per cent of char. The char contains a small amount of iron pyrites but no organic sulfur, because the latter has been hydrogenated to hydrogen sulfide. The char, while still at the reaction pressure and temperature of the hydrogenation step, can be collected in a cyclone separator and settled and transferred in an expanded state to a gasification zone where oxygen and steam are introduced. Synthesis gas produced in this way should be virtually free from sulfur and would require only a minimum of purification before use in the Fischer-Tropsch synthesis. Much additional pilot-plant operation is necessary before this combination of coal hydrogenation, char gasification, and Fischer-Tropsch synthesis can be evaluated.

[118] H. Perry, R. C. Corey, M. A. Elliott, *Continuous Gasification of Pulverized Coal with Oxygen and Steam by the Vortex Principle, A Progress Report*, presented before American Society of Mechanical Engineers, New York, November 1949.

[119] H. C. Hottel, G. C. Williams, and C. N. Satterfield, *Thermodynamic Charts for Combustion Process.* Part Two, John Wiley & Sons, 1949.

CHAPTER

5

The Oxo Process

INTRODUCTION

The word "oxo" is derived from the German term "Oxierung," meaning ketonization. The oxo reaction is the catalytic addition of carbon monoxide and hydrogen to an olefin to form aldehydes containing one more carbon atom than the olefin used. The aldehydes usually are reduced with hydrogen to primary alcohols in a second stage. This two-stage procedure is known as the oxo process. The most effective catalyst is a reactive form of cobalt such as the reduced oxide, carbonate, or acetate.

During some experiments on the effect of olefins in the feed gas in the Fischer-Tropsch process, Otto Roelen of Ruhrchemie A.G. verified the observation of Smith [1] and his coworkers that the resulting product contained large amounts of oxygenated organic compounds. Roelen [2] patented the basic procedure of the oxo process in 1938. Ruhrchemie A.G. and I.G. Farben. cooperated in the development of the process, starting about 1940. The record of the laboratory and pilot-plant work is contained in Technical Oil Mission reels 14,[3] 55,[4] and 134.[5] Summaries of this material have been published by Weir [6] and by Wender and Orchin.[7]

[1] D. F. Smith, C. O. Hawk, and P. L. Golden, *J. Am. Chem. Soc.*, **52**, 3,221–32 (1930).

[2] O. Roelen, R103,362, filed in Germany Sept. 19, 1938, corresponding to U. S. Patent 2,327,066, Aug. 17, 1943 (application date Apr. 15, 1939).

[3] T.O.M. Reel 14, Bag 3,043, Item 4, Frames 478–858.

[4] T.O.M. Reel 55, Bag 2,523, Documents 69–85, inc., and 88–93, inc.

[5] T.O.M. Reel 134, Section VII.

[6] H. M. Weir, T.O.M. Report 6, PB 2,047 (1945).

[7] I. Wender and M. Orchin, *U. S. Bur. Mines Rept. Invest.* 4,270 (1948).

CHEMISTRY OF THE PROCESS

The chief primary reaction is the addition of a formyl group, CHO, and a hydrogen atom to the olefin bond:

$$R{-}CH{=}CH_2 + H_2 + CO \rightarrow \begin{cases} R{-}CH_2{-}CH_2{-}CHO \\ RCH(CHO){-}CH_3 \end{cases}$$

Usually about 60 per cent of branched and 40 per cent of straight-chain aldehydes are obtained. In addition to the isomers from the primary addition of CO and H_2 to a particular olefin, the number of isomers in the product is further increased by a shift in the position of the olefin double bond. This shift is catalyzed by cobalt carbonyl and occurs concurrently with the primary addition of CO and H_2, as indicated:

$$R{-}CH_2{-}CH{=}CH_2 \rightleftharpoons R{-}CH{=}CH{-}CH_3$$

$$\begin{array}{ccccc} & \swarrow +H_2+CO & \searrow & \swarrow +H_2+CO & \searrow \\ R{-}CH_2{-}CH_2{-}CH_2CHO, & & R{-}CH_2{-}\underset{\displaystyle CHO}{CH}{-}CH_3, & & R{-}\underset{\displaystyle CHO}{CH}{-}CH_2{-}CH_3 \end{array}$$

The reaction that predominates is the one involving the least steric hindrance. Thus from isobutylene more $CH_3{-}\underset{\displaystyle CH_3}{CH}{-}CH_2{-}CHO$ is obtained than $CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}{-}CHO$. Similarly the trimethylpentenes (obtained from isobutylene polymerization) yield chiefly products derived from $CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}{-}CH_2{-}\overset{\displaystyle CH_3}{C}{=}CH_2$, and only very small amounts derived from its isomer, $CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}{-}CH{=}\overset{\displaystyle CH_3}{C}{-}CH_3$. Olefins with the double bond between two tertiary carbon atoms are completely unreactive in the oxo process.

A minor primary oxo reaction is the formation of ketones from two olefin molecules, as follows:

$$2R{-}CH{=}CH_2 + CO + H_2 \rightarrow \begin{cases} R{-}CH_2{-}CH_2{-}CO{-}CH_2{-}CH_2{-}R \\ R{-}CH_2{-}CH_2{-}CO{-}CH(CH_3){-}R \\ R{-}CH(CH_3){-}CO{-}CH(CH_3){-}R \end{cases}$$

The chief secondary reactions are the conversion of aldehydes to acids by way of the reaction $2R{-}CHO + H_2O \rightarrow RCH_2OH + RCOOH$, with subsequent esterification, or conversion directly to esters in the absence of water; and the aldol condensation reaction, which yields as much as 20 per cent of the total product as a high-boiling oil ("Dicköl"), which has a high hydroxyl number and is probably polyhydric in character.

An attempt [4] was made to obtain aldol condensation of oxo aldehydes at the moment of formation by adding alkaline substances and by varying the pressure and temperature. Upon subsequent hydrogenation, diols should result; or if one of the hydroxyl groups is readily split off by dehydration, a primary unsaturated alcohol should be formed. The following materials were tried: aqueous sodium hydroxide, alcoholic sodium hydroxide, sodium methylate, solid sodium hydroxide, sodium carbonate, and aqueous ammonia. No major effect in the expected direction could be found. Increase of temperature and pressure markedly increased the quantity of high-boiling material, but the hydroxyl number of the latter was low. It is suspected therefore that the increase in high-boiling material did not occur by way of the aldol condensation. A small amount (0.2 per cent of the charge) of sodium methylate was found to suppress completely the small amount of hydrogenation of the aldehydes which occurs in the first stage of the oxo synthesis. Secondary reactions proceeding to a minor extent are the formation of acetals from aldehydes and alcohols, and polymerization of the olefin to form high-boiling polymers.

The aldehydes, which are the major part of the product, are very reactive, and it is difficult to separate the components of the mixture. For preparation of individual aldehydes, it is preferable to hydrogenate the whole product, fractionate the resulting alcohols, and convert the resulting fractions to aldehyde by oxidation or dehydrogenation. The synthesis of aldehydes from olefins and $CO + H_2$ in the first stage of the oxo process appears to be a homogeneous catalytic reaction. Thus,

its rate is not affected by appreciable amounts of sulfur compounds,[4] whereas aqueous ammonia completely inhibits the synthesis,[4] presumably by the formation of cobalt-ammonia complex and consequent destruction of the active catalyst, which probably is cobalt hydrocarbonyl.

Concurrently with the synthesis of aldehydes, a catalytic shifting of the double bond in the olefin occurs. At Leuna in 1942, Ansinger and Berg [8] studied the shifting of the double bond in pure dodecene-1 at various temperatures with different catalysts. The experiments were done in a small autoclave with a preheating time of 1 hr, and with 1 hr at reaction temperature. To remove metal carbonyl the product was treated with 5 per cent sulfuric acid at 50°C and distilled. The isomeric composition was determined by forming the ozonide, treating it with silver oxide and sodium hydroxide, and subsequently identifying the products of the resulting splitting reaction. The results are given in Table 1. The following conclusions are based on the results given in

TABLE 1. EXPERIMENTS SHOWING MIGRATION OF THE DOUBLE BOND IN DODECENE-1

Experiment	Dodecylene, cc	Catalyst	Reaction Temperature, °C	Gas Used	Pressure, atm	Position of Double Bond from End Carbon Atom, mole per cent					
						1	2	3	4	5	6
1	395	Fischer,[a] 100 cc	200	N_2	200	100	....	....	....	....	....
2	395	Fischer,[a] 100 cc	300	N_2	200	7.0	45.5	30.1	8.3	5.8	3.0
3	265	Fischer,[a] 200 cc	250	CO	100	3.0	15.0	20.0	22.0	21.0	18.5
4	265	Cobalt metal, 20 g	150	CO	100	3.0	24.0	25.0	18.0	16.0	13.5
5	265	Fischer,[a] 200 cc	150	CO	100	8.1	27.2	23.0	18.1	13.3	10.3
6	265	Iron pentacarbonyl, 65 g	150	CO	100	58.2	17.8	8.9	5.7	5.1	4.2
7	265	Nickel metal, 20 g	150	CO	75	100	....	....	....	....	....

[a] Reduced Ruhrchemie catalyst of approximately the following parts by weight: 100Co:5ThO_2:8MgO:200 kieselguhr, 1–3-mm granules.

Table 1 and on other known facts concerning the oxo synthesis. The Ruhrchemie (Fischer) catalyst, 100Co:5ThO_2:8MgO:200 kieselguhr, does not cause shifting of the double bond at 200°C in a nitrogen atmosphere, but does so at 300°C. A small amount of cyclization also occurs at 300°C. As the oxo synthesis is operated at about 150°C, it is apparent that Fischer catalyst, in the absence of CO, is not effective in causing migration of the double bond. Experiments 4 and 5 show that cobalt metal (from reduction with hydrogen of cobalt oxide at 400°C and 200 atm) and reduced Ruhrchemie Fischer-Tropsch catalyst are

[8] Reference 5, Item 6.

quite effective at 150°C in the presence of CO; the product contains substantial portions of all possible isomers produced by double-bond migration. Iron pentacarbonyl at 150°C and 100 atm of CO also is effective, but to a much smaller extent than cobalt. Nickel is entirely ineffective at 150°C and 100 atm of CO. It is of interest that the order of effectiveness of cobalt, iron, and nickel in the oxo synthesis is about the same as in the isomerization of olefins by double-bond migration. The fact that the degree of branching of oxo aldehydes is not as great as would be expected from the extent of double-bond migration shown in Table 1 can be explained by assuming that the isomerization rate is somewhat lower than the rate of addition of CO and H_2 to the double bond.

The alcohols produced in the synol process (Chapter 4, p 395) are largely unbranched. This fact has been used by Ansinger and Berg [8] as evidence against the assumption of an oxo-type reaction occurring in the synol process. However, it is conceivable that the orienting influence on an oxo reaction of the catalytic surface of a fused iron catalyst, under conditions where only surface films of iron carbonyl are present, is sufficient to account for the absence of extensive branching in the synol product.

Recent experiments by Wender, Levine, and Orchin [9] showed that butyraldehyde and heptaldehyde are readily reduced to butanol and heptanol, respectively, by treatment with $1H_2 + 1CO$ gas at 160°C and at 3,000–4,000 psi in the presence of cobaltous acetate, which was powdered and mechanically dispersed in the aldehyde. It was found also that furan and 2,5-dimethyl furan when subjected to the oxo reaction yielded tetrahydrofurfuryl and 2,5-dimethyl-3-tetrahydrofurfuryl carbinol. It was further found that exhaustive treatment of olefins such as hexene with synthesis gas under the usual oxo conditions gave heptanol and that no aldehyde was present in the product.

Wender, Levine, and Orchin [9] discovered also that an alcohol reacts with $1H_2 + 1CO$ gas at 160°–180°C and at 3,000–4,000 psi in the presence of cobaltous acetate to form an alcohol with one more carbon atom. When the contact time was extended for several hours a number of homologous alcohols of higher carbon content were formed. These findings probably will result in some basic changes in the oxo or hydroformylation process.

[9] I. Wender, R. Levine, and M. Orchin, *The Mechanism of the Oxo and Related Reactions.* I. *The Direct Production of Alcohols in the Oxo Reaction*, presented before the American Chemical Society, Atlantic City, N. J., September 1949; II. *Homologation of Alcohols*, *J. Am. Chem. Soc.*, **71**, 4,160 (1949).

HYDROFORMYLATION OF PURE OLEFINS

Ethylene [10] was reacted in water or toluene solution. The I.G. Farben. used water as solvent, at 150°–200°C reaction temperature and at 150–300 atm. The feed gas contained equal volumes of CO, H_2, and C_2H_4. The rate of water circulation was such as to give an effluent containing 2–3 per cent of propionaldehyde, which was removed by distillation and the water recirculated. The product composition was 65 per cent propionaldehyde, 20–25 per cent ethane, and 10–15 per cent secondary products, such as polymers of propionaldehyde. The reactor was packed with pumice on which 0.5–1 per cent of cobalt had been deposited, and depletion of cobalt was compensated for by addition of cobalt salts of fatty acids to the feed water.

Ruhrchemie used toluene as solvent because it is readily separated from the oxo products. The operating temperature and pressure were, respectively, 115°C and 150 atm. Through a suspension of 5–7 per cent of Ruhrchemie cobalt catalyst in toluene, a feed gas containing 25 per cent C_2H_4, 25 per cent CO, and 35 per cent H_2 was pumped at the rate of 18 cu m per hr. The residual gas was virtually free from ethylene and emerged at the rate of 4–5 cu m per hr. The product contained 70–80 per cent propionaldehyde and other products such as ethane, methyl ethyl acrolein, and diethyl ketone.

If the temperature was increased, a small amount of product characteristic of the Fischer-Tropsch synthesis was obtained, but the main change was the production of propanol instead of the aldehyde. Roelen stated [10] that this direct alcohol synthesis could be carried out by passing water gas-ethylene mixture over a fixed cobalt catalyst supported on pumice at about 210°C, the products being chiefly propanol and ethane. Roelen did not state the operating pressure. No cobalt carbonyl appeared in the products. The catalyst operated 1,000 hr without any deterioration. Roelen stated that a direct alcohol synthesis of this type can be conducted with higher olefins, but the proportion hydrogenated directly to the hydrocarbon increases with molecular weight. Recent unpublished work in research laboratories in the United States shows that very little hydrogenation of aliphatic olefins occurs during the hydroformylation reaction.

Propylene [10] yields chiefly equal amounts of butyraldehyde, $CH_3—CH_2—CH_2—CHO$, and dimethyl acetaldehyde, $CH(CH_3)_2—CHO$. Isobutylene [11] yields about 80 per cent of 3-methylbutanol-1 and 20 per

[10] C. C. Hall, S. R. Craxford, and D. Gall, Interrogation of Dr. Otto Roelen of Ruhrchemie A.G., *B.I.O.S. Final Rept.* 447, Item 30; PB 77,705.

[11] T.O.M. Reel 36, Items 21 and 36, I.G. Farben., Patent Applic. OZ 13,669.

cent of higher-boiling alcohols, from the two-stage process (hydroformylation followed by hydrogenation). No 2,2,2-trimethylethanol was formed.

2-Methylpentene-1 was subjected to the oxo reaction by Eckhardt.[12] The product was chiefly 3-methyl hexaldehyde and includes smaller amounts of 3-methyl hexanol-1, 3-methylcaproic acid, 2,8-dimethyl undecanone-6, some C_{14} aldehyde and C_{14} carboxylic acid, higher esters of β-methylcaproic acid, and some β-methyl caproaldehyde dimethyl acetal (when methanol is added to the reaction mixture).

Cyclohexene yielded [12,13] chiefly (90 per cent) hexahydrobenzaldehyde and hexahydrobenzyl alcohol. The remaining 10 per cent of the product contained a major amount of dimeric hexahydrobenzaldehyde and smaller amounts of trimeric hexahydrobenzaldehyde.

Starting with cyclohexene, a major proportion (about 75 per cent) of the product may be obtained as hexahydrobenzyl alcohol. This can be dehydrated to yield methylenecyclohexane. The latter, when used in the oxo synthesis, yields β-cyclohexylethyl alcohol, which upon dehydration gives cyclohexylethylene, a valuable raw material for plastics manufacture. Partially reduced aromatic rings undergo the oxo reaction. However, attempts to build up the higher alcohols further in a series of oxo reactions and dehydrations were not successful probably because of extensive formation of branched-chain olefins.

n-Dodecylene yields,[14] upon hydroformylation and hydrogenation of the aldehyde, tridecyl alcohol containing about 40 per cent of the normal alcohol and 60 per cent of alkyl branched alcohols (dialkyl ethanols).

Adkins and Krsek [15] investigated hydroformylation of several types of unsaturated compounds containing one double bond, at 125°C and 100–300 atm of $1H_2 + 1CO$, in the presence of dicobalt octacarbonyl as catalyst. The nature of the radical R in substituted ethylenes $R—CH=CH_2$ exercised a marked influence on the place of addition of the —CHO group. Thus, when R was $—CO_2C_2H_5$, $—CH_2O_2CCH_3$, or $—CH(O_2CCH_3)_2$, or when $(C_2H_5)_2C=CH_2$ or $C_2H_5C(CH_3)=CH_2$ was the reactant, addition of —HCO was exclusively to the terminal carbon atom. In contrast to these results, when R was phenyl, α-naphthyl, ethoxymethyl, or *n*-butoxy, addition of —HCO was on the substituted carbon atom, and good yields of aldehydes of the structure $RCH(CH_3)$-CHO were obtained. When R was n-C_4H_9—, n-$C_{16}H_{33}$—, $—(CH_2)_8$-CO_2CH_3, $—CH_2OC_6H_5$, $—CH_2OC_2H_5$, or $—O_2CCH_3$, the addition of

[12] Reference 5, Item 7.
[13] Reference 5, Item 1.
[14] T.O.M. Reel 134, Section 7, Item 3.
[15] H. Adkins and G. Krsek, *J. Am. Chem. Soc.*, **71**, 3,051–5 (1949).

—HCO gave mixtures of aldehydes of the types RCH_2CH_2CHO and $RCH(CH_3)CHO$.

Crotonaldehyde, acrolein, methyl vinyl ketone, and mesityl oxide, all of which contain an α,β-unsaturated carbonyl system, were reduced to the corresponding saturated carbonyl compounds yielding, respectively, butyraldehyde, propionaldehyde, methyl ethyl ketone, and methyl isobutyl ketone. Apparently α,β-unsaturated aldehydes and ketones cannot undergo the hydroformylation reaction.

HYDROFORMYLATION OF PURE DIOLEFINS

The dimethylhexadienes were subjected to the oxo reaction by Gemassmer, Berg, and Meusel [16] of the I.G. Farben. 2,5-Dimethyl-

$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_2{-}CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2$$

hexadiene-1,5, dissolved in four times its volume of cyclohexane, reacted readily, yielding a mixture of nonanol and decanediol, the latter constituting 35 per cent of the product. Various unsuccessful attempts were made to repress the formation of the nonanol and increase the yield of decanediol. These attempts included increasing the carbon monoxide partial pressure, operating at the lowest possible temperature, addition of carbon disulfide to repress hydrogenation, use of paraformaldehyde in place of $CO + H_2$, and use of methanol as a solvent. Mixtures of CO and H_2O or CO and alcohol were tried in place of $CO + H_2$ with the hope of obtaining a good yield of dimethyl suberic acid or of its ester. However, no conversion at all occurred when water or alcohol replaced the hydrogen.

The conjugated diolefin, 3,4-dimethylhexadiene-2,4,

$$CH_3{-}CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}CH_3$$

gave an almost quantitative yield of nonanol and no diol. It was suspected that the 2,5-dimethylhexadiene-1,5 formed only 35 per cent diol because it contained substantial amounts of the conjugated isomer. Careful physical measurements, however, showed that this was not the case.

Dimethallyl sulfide and dimethallyl ether [17] were subjected to the oxo reaction. High diol yield was expected because the sulfur or the oxygen atom should prevent the double-bond migration to form a conjugated

[16] Reference 4, Documents 78, 79, 80, 81.

[17] Reference 4, Document 74.

system. Both substances, however, when dissolved in cyclohexane and subjected to the oxo conditions, reacted in a complex manner. The boiling points obtained upon distillation of the products increased gradually from 100° to 400°C, and each fraction had a very small hydroxyl number.

HYDROFORMYLATION OF FISCHER-TROPSCH PRODUCTS

Products from the various types of Fischer-Tropsch operations were subjected to the oxo synthesis by Gemassmer and Berg.[18] The proximate analysis of the raw materials and of the products was done by fractional distillation and determination of hydroxyl numbers, iodine numbers, etc., on these fractions. In all cases, about 95 per cent of the olefins in the raw material was converted to alcohol. The product of the Ruhrchemie operation with end-gas recycle on cobalt catalyst (see Table 38 of Chapter 4) was particularly well suited for use in the oxo process, because of the high yield of alcohol suitable for either detergent or plasticizer[19] production. The alcohol product was colorless and odorless.

Olefinic gasols and gasolines from cracking of German, Hungarian, and Rumanian petroleum, shale oils from Estonian and Swedish operations, low-temperature-carbonization brown-coal tars, and liquid-phase coal-hydrogenation oils also were subjected to the oxo process. In most cases the oxo reaction could be effected without preliminary refining of the oil. Pretreatment with caustic and with dilute acids was found desirable for the brown-coal tar. Somewhat higher than normal temperatures were needed for hydroformylation of olefins from petroleum products, but otherwise the reaction proceeded smoothly. Hydrogenation was retarded somewhat by the presence of sulfur compounds. The alcohols formed were separated in part by distillation and in part by way of the boric acid esters.[20] The alcohols usually were clear or pale yellow liquids with a faintly aromatic odor. They had low melting points and surprisingly high densities, which probably were due to the presence of cyclic components. The sulfates prepared from these products and chlorosulfonic acid were good detergents.

[18] Reference 5, Item 5.

[19] Reference 3, Frames 798–801.

[20] T.O.M. Reel 134, Section II, Item 23, contains data on the separation of aliphatic alcohols from accompanying hydrocarbons by extraction with aqueous methanol.

LARGE-SCALE OXO-PROCESS DEVELOPMENT

Characteristics of the Process of Importance in Process Development

The temperature in the hydroformylation stage varies from 115° to 190°C, depending upon the catalyst activity and the nature of the olefinic raw material. The choice of reaction temperature was also determined by the extent of isomerization desired in the product. Thus, if the hydroformylation of a C_{16} olefin was started and maintained at 170°–190°C, the alcohols obtained by hydrogenation of the product had a low melting point, whereas when the hydroformylation was started at 100°–130°C and the temperature slowly raised, the alcohols had an appreciably higher melting point.

Although hydroformylation of olefins could be conducted at moderate pressures of about 50 atm, only about 10 per cent conversion was obtained in 1 hr, whereas at 150 atm 70–80 per cent conversion was obtained. The reaction is exothermic (about 150 kcal per kg of olefin charged for the total reaction to produce alcohols), and adequate arrangements for temperature control must be made.[16,21] After completion of the hydroformylation, the liquid aldehyde plus the catalyst suspended in it must be cooled under pressure. If the pressure is lowered before cooling, cobalt metal from the decomposition of cobalt carbonyl deposits immediately beyond the point of pressure release.[21]

Although the oxo reaction is not sensitive to sulfur compounds, the catalytic hydrogenation of oxo aldehydes is greatly retarded by sulfur compounds and carbon monoxide. It was therefore considered necessary to reduce to a minimum the amount of cobalt carbonyl carried by the oxo liquids into the hydrogenation stage, and to avoid increase in the CO content of the recycled hydrogen. The latter was achieved by introduction of a methanation step in the recycle hydrogen stream, whereby the CO was converted to methane by passage of the gas mixture over an iron or nickel catalyst.

Batch Processes of Ruhrchemie and I.G. Farben.

At Leuna,[22] in experimental batch operations, six vertical reactors 20 cm I.D. and 800 cm high were used. They were jacketed (water under pressure) and contained a tubular heat exchanger. A batch of 140 l of liquid olefin plus 4 per cent of Ruhrchemie cobalt catalyst was

[21] Reference 4, Documents 72, 73, 78, 79.

[22] Reference 5, Item 2.

heated to reaction temperature (125°–150°C) under 150 atm of water gas. Effective agitation was accomplished by passing 60 cu m per hr of water gas through the reactor. After about 1 hr the reactor contents were cooled and discharged at atmospheric pressure. The liquid plus catalyst was then pumped into a second converter and hydrogenated at 180 atm of hydrogen and at about 180°C. About 60 cu m per hr of hydrogen was passed through the reactor. The product from the hydrogenation stage was filtered, and the catalyst thus recovered was recycled to the hydroformylation stage.

This batch operation at Leuna showed that the abrasive Ruhrchemie cobalt catalyst can be pumped at high pressure without too much erosion on pumps and valves. Only the valves discharging the slurry to atmospheric pressure were appreciably eroded, and here Widia valves (tungsten carbide seats and needles) were used.

At Oberhausen-Holten,[23] the Ruhrchemie batch operation was conducted in 40-cm-I.D. reactors 1,200 cm high. Each reactor contained a heat exchanger consisting of thirty-one tubes, 38 mm O.D. and 800 cm long. The heat exchangers were connected to a steam drum. The operation was similar to that described for the Leuna batch operation.

Designs for Continuously Operating Plants

The continuous operation at Leuna was described by Horne[24] and discussed in a conference[25] at Oberhausen-Holten in 1943. Four per cent of powdered, reduced Ruhrchemie cobalt catalyst was added to the olefinic raw material. Most of the catalyst was recycled from the filters after the second (hydrogenation) stage of the process. Three hundred to 700 l of this slurry was preheated to about 150°C and pumped into the first reactor concurrently with 15–20 cu m per hr of purified, preheated (to 150°–190°C) water gas and 40–45 cu m per hr of recycled water gas, at 220–240 atm. The first reactor was 20 cm I.D. and 800 cm high and was constructed of carbon steel. It contained six steel cooling tubes 21 mm O.D., 17 mm I.D., which were connected to a water jacket surrounding the reactor, and both tubes and jacket were connected into a steam boiler. Cooling by these tubes was used only when very reactive olefins were charged and the heat release was large. The temperature of product from the first reactor was maintained at about

[23] Reference 5, Item 10.

[24] Report on the Investigation by Fuels and Lubricants Teams at the I.G. Farben. A.G., Leuna Works, Merseburg, Germany, PB 6,650; *U. S. Bur. Mines Inform. Circ.* 7,370 (1946), pp 89–92.

[25] Reference 5, Item 17.

150°C. The temperature and feed rate depended upon the concentration and molecular weight of olefins in the feed. About 70 per cent of the olefins usually were converted in the first reactor.

The products from the top of the first reactor were conducted into the bottom of the second, concurrently with an additional 60 cu m per hr of preheated water gas. The second reactor had the same dimensions as the first but was fitted with baffles and did not contain any cooling tubes. The usual temperature in the second reactor was 170°C. Virtually all the remaining olefins were hydroformylated, and about 20 per cent of the aldehyde product was hydrogenated to alcohol.

The products from the top of the second reactor flowed through a water cooler and thence to a separator, where the liquid product was separated from the excess water gas. Both cooler and separator were at reaction pressure (220–240 atm). Cobalt carbonyl had to be completely removed from the recycled water gas to avoid the formation of cobalt deposits in the gas preheaters. The recycle gas was scrubbed under pressure by crude alcohol product fed into a bubble-cap column.[26] The liquid product from the separator was let down to atmospheric pressure, and the released dissolved gases were purged after scrubbing with alcohol product to prevent loss of liquid by entrainment. When low-molecular-weight (C_2–C_8) olefins were hydroformylated, the released dissolved gases were passed through activated charcoal or silica gel to recover product vapors.

The first-stage liquid product was preheated and pumped concurrently with 60 cu m per hr of a preheated mixture of fresh hydrogen and methanized recycle hydrogen at 200–250 atm into the bottom of the first reactor of the second stage. This reactor was identical in construction with the first reactor of the first stage. The temperature of the product coming from the top of the first hydrogenation reactor was maintained at 180°C. The product was conducted into the top of the second hydrogenation reactor, where it flowed countercurrently to a stream of 60 cu m per hr of a preheated mixture of fresh and recycle hydrogen. The second hydrogenation reactor was identical in construction with the second hydroformylation reactor. Liquid product was discharged from the bottom of the second hydrogenation reactor at such a rate as to keep the reactor about three-fourths full of liquid and provide a gas cushion at the top from which hydrogen containing some carbon monoxide was withdrawn. This gas was water-cooled and passed to a catch pot for separation of condensed liquid which was returned to the hydrogenation reactor. Before being recycled, gas from the catch pot

[26] Reference 5, Item 11.

was heated to 250°C and passed over an iron (synthetic-ammonia-type) catalyst for conversion of carbon monoxide to methane.

The liquid product was let down to about 10 atm in a separator from which the liberated dissolved gases were vented. It was then filtered in batches of 700 l in a pressure filter equipped with porous ceramic tubes. The catalyst was washed off the tubes by olefin feed stock and recycled to the first-stage feed pumps.

A number of variations in the Leuna continuous process were tested. The effect of introducing liquid feed at the top instead of the bottom of one or both of the first-stage reactors, and of countercurrent flow of liquid and gas in the first stage, was tried. The process also was operated with only one reactor in each stage. All these variations proved less efficient than the procedure outlined above. Any appreciable decrease in recycling of gas through the reactors resulted in inadequate agitation of the slurry of catalyst and liquid reactant.

At Ludwigshafen [25] the oxo synthesis was conducted in reactors packed with granules of pumice impregnated with a cobalt compound. Depletion of cobalt in the pumice was made up by recycling a cobalt compound soluble in the olefin feed. All the heat of reaction was removed by gas recycling through heat exchangers outside the converters. The cobalt compound was prepared by treatment of cobalt acetate with commercial fatty acids characterized [25] as "first runnings." The displaced acetic acid was separated in a vacuum evaporator, and the fatty acid salt of cobalt was dissolved in the olefin feed to yield a cobalt concentration of 0.02–0.05 per cent. This solution was pumped through a preheater to the top of the first reactor and was passed down through it concurrently with a mixture of preheated fresh and recycled water gas. The liquid flow in the second hydroformylation reactor also was downward, concurrent with the gas flow. The rate of gas flow was about 14,000 volumes per volume of catalyst packing per hour in both the hydroformylation and hydrogenation stages. The off gas from each reactor was passed through a heat exchanger to remove the heat of reaction. The liquid product from the first stage was passed along with hydrogen through a decobalting reactor packed with pumice. Here the cobalt carbonyl was reduced to cobalt, which precipitated on the packing and was periodically reconverted to carbonyl by use of carbon monoxide. The recovered carbonyl was fed into the olefin feed to the first stage. The decobalted liquid product from the first stage was sent to the hydrogenation stage. The latter was identical with the oxo stage, except that the reactors were packed with granules of an efficient reducing catalyst. It appears probable from the discussion [25] in the minutes of the conference that the Ludwigshafen procedure had not been

tested on a pilot-plant scale and was based on relatively small laboratory experiments. A plant of this type probably would be more costly to install and operate than the Leuna continuous plant because of the appreciably larger number of high-pressure vessels, such as separators, and heat exchangers.

The Isoparaffin Synthesis

INTRODUCTION

The synthesis of highly branched aliphatic hydrocarbons from water gas was developed on a laboratory scale at the Kaiser Wilhelm Institut für Kohlenforschung in Mülheim, Germany, by Pichler and Ziesecke.[27] Non-reducible oxides, particularly thoria, were found to catalyze the reduction of carbon monoxide at elevated temperatures (about 450°C) and pressures (100–1,000 atm). The product contained chiefly branched-chain aliphatic hydrocarbons, and only minor amounts of normal paraffins. Under these conditions Fischer-Tropsch catalysts (promoted iron or cobalt) yield chiefly carbon and methane. Methanol synthesis catalysts (such as copper-zinc oxide) yield chiefly oxygenated compounds and small amounts of hydrocarbons.

CATALYST PREPARATION

Most of the catalysts were prepared by precipitation from nitrate solutions by addition of sodium carbonate. The thorium catalyst used in most of the experiments ("standard" catalyst) was prepared by adding a boiling solution of sodium carbonate to an equal volume of boiling solution of thorium nitrate containing 120 g of thorium nitrate per l. A slight excess of sodium carbonate was present. The precipitate was washed free of excess alkali and dried at 110°C. This procedure yielded a hard, granular catalyst whose bulk density was 1.3. If more concentrated solutions were used, the catalysts had a lower bulk density. Thus, with 360 g of thorium nitrate per l and a corresponding three-fold increase in sodium carbonate concentration, the catalyst obtained had a bulk density of only 0.76 and was much softer. When a concentration of 120 g of thorium nitrate per l was used and the precipitation was conducted very slowly, *eg*, over a period of 1 hr, the resulting catalyst was a dense, glassy material of 2.3 bulk density. Similarly dense catalysts were obtained even with rapid precipitation when sodium hydroxide or ammonia was used as precipitant. The standard catalyst of bulk density 1.3

[27] H. Pichler and K. H. Ziesecke, The Isoparaffin Synthesis, T.O.M. Reel 279, Frames 790–931; translation published in *U. S. Bur. Mines Bull.* 488 (1950), 34 pp.

usually was heated at 300°C for some time before use in the synthesis. This heating resulted in the evolution of water and carbon dioxide, with concurrent shrinkage and increase in bulk density to 2.0.

The thoria catalyst was unaffected by sulfur compounds. Neither preliminary treatment with hydrogen sulfide or carbon disulfide nor precipitation with ammonium sulfide had any effect on its activity. In addition to this insensitivity to sulfur, the thoria catalyst was a very durable one. Periodic burning off of carbon deposits in air at synthesis temperature did not impair its activity.

APPARATUS USED IN THE TESTS

The reaction vessel was a copper-lined steel tube about 1 cm in diameter and 50 cm long. Ordinary or low alloy steels are catalytically active in production of appreciable amounts of carbon and methane. It was desirable, therefore, to use stainless or high alloy steels if the copper liner was not used. In most of the tests 25 cc of catalyst was spread over a 30-cm length of the reactor which was in a slightly inclined (about 15°) position from the horizontal. The products passed through a liquid-gas separator under pressure. The pressure then was reduced to atmospheric, and the gas conducted through a bed of activated charcoal and a gas meter. In most of the experiments the reactants made a single pass (no recycle of end gas) through the reactor. The off-gas velocity was in all cases 10 l per hr. In some experiments the end gas was recycled after being passed through two liquid-gas separators under pressure, one at atmospheric temperature and the other at −25°C.

CATALYST ACTIVITY TESTS

Activity tests were made on a large number of unpromoted oxides. The oxides of thorium, aluminum, chromium, titanium, beryllium, zirconium, uranium, zinc, manganese, magnesium, cerium, and lanthanum were tested. Of these, thorium oxide, zirconium oxide, and to a small extent cerium oxide were active catalysts for the synthesis of isoparaffins. The product from alumina included large amounts of methane and carbon, although some isoparaffins were present. Table 2 contains results of tests with ThO_2, ZrO_2, CeO_2, and Al_2O_3. The remaining oxides, as well as preparations of alumina obtained by various procedures, either were poorly active or produced chiefly methane and carbon.

The effect of potassium carbonate as a promoter for thoria was determined. The washed thoria precipitate was repulped with water containing a measured quantity of potassium carbonate, and the mixture

evaporated to dryness. Comparative tests were made at 30 atm and at 450°, 475°, and 500°C. Thoria catalysts containing 0, 0.5, 1.0, 5.0, and 25 per cent of potassium carbonate were tested. The results show that the activity of the thoria decreased with increasing alkali content, the decrease being greater at the lower temperatures. Thus, upon increasing the alkali content from 1 to 5 per cent the conversion at 450°C dropped from 13 to almost zero per cent, whereas at 500°C it dropped only from 28 to 22 per cent. Thus, it was possible with alkalized thoria to conduct the synthesis at 500°C without extensive formation of carbon and

Table 2. Activity of Unpromoted Thoria, Zirconia, Ceria, and Alumina at 450°C, 150 atm of Water Gas ($1H_2 + 1CO$)

Catalyst	Gas Conversion, volume per cent	Per Cent Isobutane in the C_4 Fraction	Grams per Cubic Meter of Water Gas	
			Isobutane	Oil + Gasoline
ThO_2	46	88	16	40
ZrO_2	32	82	9	..
CeO_2	10	81	1.3	..
Al_2O_3	53	59	2.8	5

methane. At 500°C the products were largely cyclic hydrocarbons. For example, at 30 atm and 500°C, the liquid hydrocarbons produced when a thoria catalyst containing 1 per cent potassium carbonate was used contained 42 per cent of naphthenes, 8 per cent of aromatics (principally toluene), and 3 per cent of phenol. At 450°C and 300 atm, small amounts of alkali (about 0.5 per cent of potassium carbonate) did not affect the degree of conversion, but altered the product distribution so that a larger proportion of higher-boiling hydrocarbons was produced.

Alumina, chromium oxide, and zinc oxide were found to be desirable promoters for thoria in the isoparaffin synthesis. The best results with alumina were obtained when the thoria and alumina were precipitated separately and the washed precipitates mixed before drying and sintering at 300°C. The alumina was precipitated from sodium aluminate solution by acidification with sulfuric or carbonic acids. The thoria was precipitated from nitrate solution by addition of sodium carbonate solution. Table 3 contains results of tests with different amounts of alumina in a coprecipitated ThO_2-Al_2O_3 catalyst, and data for comparison of coprecipitated and separately precipitated $1.0ThO_2:0.2Al_2O_3$ catalysts as well as for comparison of 0.2 and 0.6 per cent K_2CO_3 in separately precipitated $1.0ThO_2:0.2Al_2O_3$ catalysts. The K_2CO_3 was added to the washed alumina before mixing with the thoria. Alumina increased the yield of isobutane and of methane and decreased that of liquid hydro-

TABLE 3. ACTIVITY OF ThO_2-Al_2O_3 AND ThO_2-Al_2O_3-K_2O CATALYSTS AT 450°C AND 300 ATM OF $1CO + 1H_2$ GAS

Weight Per Cent of ThO_2		Method of Catalyst Preparation	Conversion, per cent of		Grams per Cubic Meter of $CO + H_2$ Feed Gas							
					Liquid Hydrocarbons	Alcohols		Hydrocarbons				
Al_2O_3	K_2CO_3		CO	H_2		In Oil Layer	In Water Layer	*i*-C_4	*n*-C_4	C_3	C_2	C_1
0	0	[a]	61	47	42.2	8.6	10.7	22.7	3.2	10.9	4.2	11.1
10	0	Copreeipitation	59	51	32.8	3.3	12.6	37.6	5.4	5.5	2.7	13.2
20	0	Coprecipitation	64	60	21.0	1.2	11.8	47.2	6.1	4.8	2.2	26.9
20	0	Separate precipitation	73	67	34.1	1.0	2.3	60.5	9.0	8.6	10.2	14.8
20	0.2	Separate	72	68	34.9	0.0	1.2	67.4	10.1	0.0	8.6	15.8
20	0.6	Separate	78	75	25.4	0.0	0.2	84.6	9.8	0.0	7.3	21.5

[a] Pure thoria.

carbons and of oil-soluble alcohol. Addition of potassium carbonate further increased the isobutane yield. The liquid product from the thoria catalyst containing 20 per cent alumina and 0.6 per cent potassium carbonate contained about 40 per cent of isopentane.

As shown in Table 4, thoria-zinc oxide catalysts yielded a larger proportion of liquid hydrocarbons than thoria-alumina catalysts. The

TABLE 4. ACTIVITY OF ThO_2-ZnO CATALYSTS AT 450°C AND 300 ATM (10 L OF END GAS PER 28 G OF ThO_2 PER HR, 2–4-MM GRANULES OF CATALYST

Catalyst, weight per cent of		Method of Catalyst Preparation	H_2:CO Ratio in Feed Gas	Conversion, per cent of		Grams per Cubic Meter of $CO + H_2$ Feed Gas						
						Liquid Hydrocarbons	Alcohols		Hydrocarbons			
ThO_2	ZnO			CO	H_2		In Oil Layer	In Water Layer	*i*-C_4	*n*-C_4 + C_3	C_2	C_1
0	100	Na_2CO_3 (aq) to $Zn(NO_3)_2$ (aq)	1.2	38	41	0.0	6.9	23.1	1.9	1.4	2.0	51
100	0	Na_2CO_3 (aq) to $Th(NO_3)_4$ (aq)	1.0	61	47	42.2	8.6	10.7	22.7	14.1	4.2	11.1
75	25	Na_2CO_3 (aq) to nitrate solution	1.25	70	67	30.7	5.6	10.1	31.7	14.5	7.7	22.3
75	25	Nitrate solution to Na_2CO_3 (aq)	1.25	74	55	50.3	6.0	8.9	26.9	21.8	6.1	10.3
75	25	Nitrate solution to Na_2CO_3 (aq)	0.88	77	69	78.7	2.6	5.8	19.3	21.8	4.6	9.9

thoria-zinc oxide catalysts were prepared by precipitation from nitrate solutions by addition of sodium carbonate. The mode of precipitation was important, particularly the order in which the nitrate and soda solutions were mixed. Catalysts prepared by addition of the boiling nitrate solution to the boiling soda solution yielded a larger proportion of liquid products than catalysts prepared by addition of the soda solution to the nitrate solution. The precipitated thoria-zinc oxide was washed free of excess alkali, dried at 110°C, and heated in air at 300°C.

Thoria-chromium oxide catalysts were active but somewhat less so than thoria-alumina or thoria-zinc oxide. Thoria-zinc oxide-alumina catalysts were of about the same activity as thoria-zinc oxide. Zinc oxide-alumina and alumina-chromium oxide catalysts were much less active than the thoria catalysts. Addition of as little as 0.25 per cent of iron to thoria resulted in a very large production of methane. Addition of 10 per cent of silica (kieselguhr was used) to a thoria-alumina catalyst increased the methane production to about three times that of the silica-free catalyst.

EFFECT OF TEMPERATURE ON PRODUCT DISTRIBUTION, USING STANDARD THORIA CATALYST, 150 ATM PRESSURE OF $1CO + 1H_2$ GAS

Figure 1 shows the change in character of the product with temperature. Below 375°C the product was chiefly alcoholic in nature, and above 500°C the proportion of gaseous hydrocarbons was large. In the range 375°–475°C isoparaffins constituted the major portion of the product.

EFFECT OF PRESSURE ON PRODUCT DISTRIBUTION, USING STANDARD THORIA CATALYST AT 450°C, AND $1CO + 1H_2$ GAS

Figure 2 shows the change in amount and character of the product with pressure. Below 100 atm the total yield was low, being about 50 g per cu m at 75 atm; and gaseous hydrocarbons constituted 30–50 per cent of the product. Above 100 atm the total yield and the proportion of liquid hydrocarbons increased rapidly with pressure. In obtaining the data used for construction of the curves of Figure 2, the flow of end gas was the same (10 l per 28 g thoria per hr, measured at atmospheric pressure and temperature) for all pressures. The contact time increased, therefore, directly with the operating pressure. To estimate separately

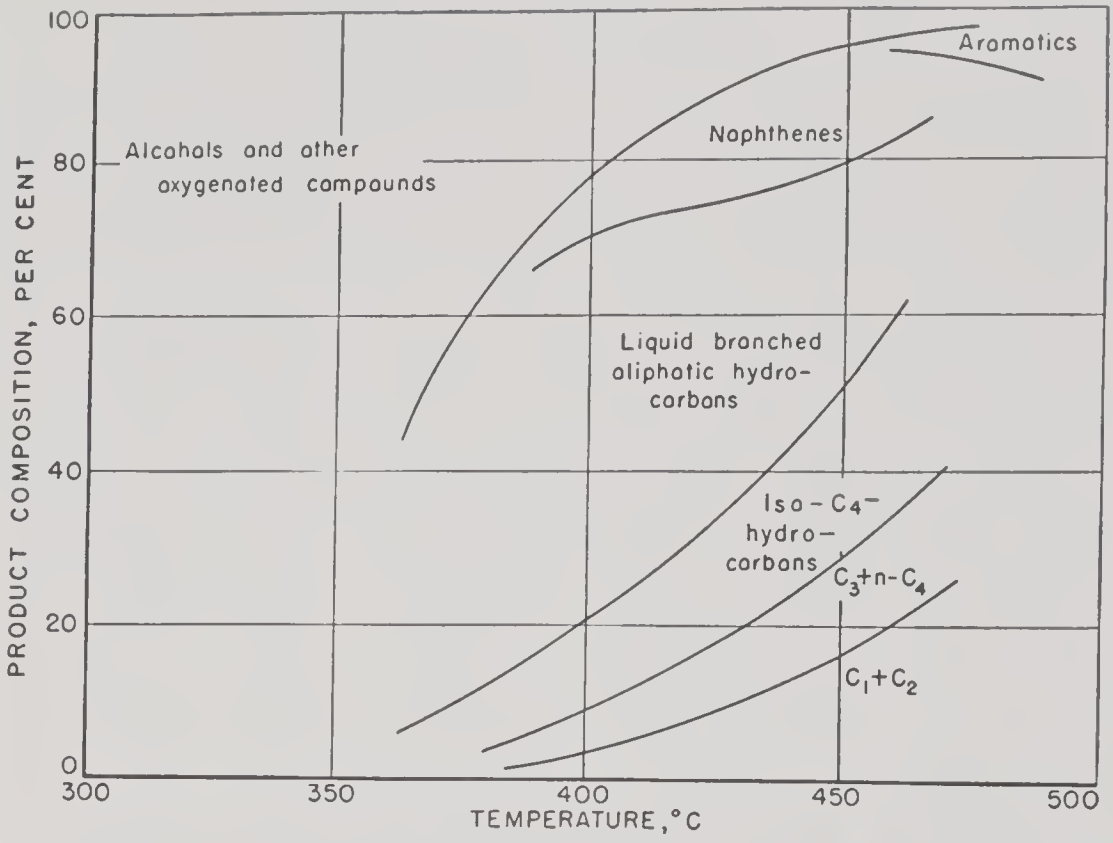


FIGURE 5–1. Reaction-product composition as related to temperature (ThO_2 single-component catalysts). Reproduced from reference 27.

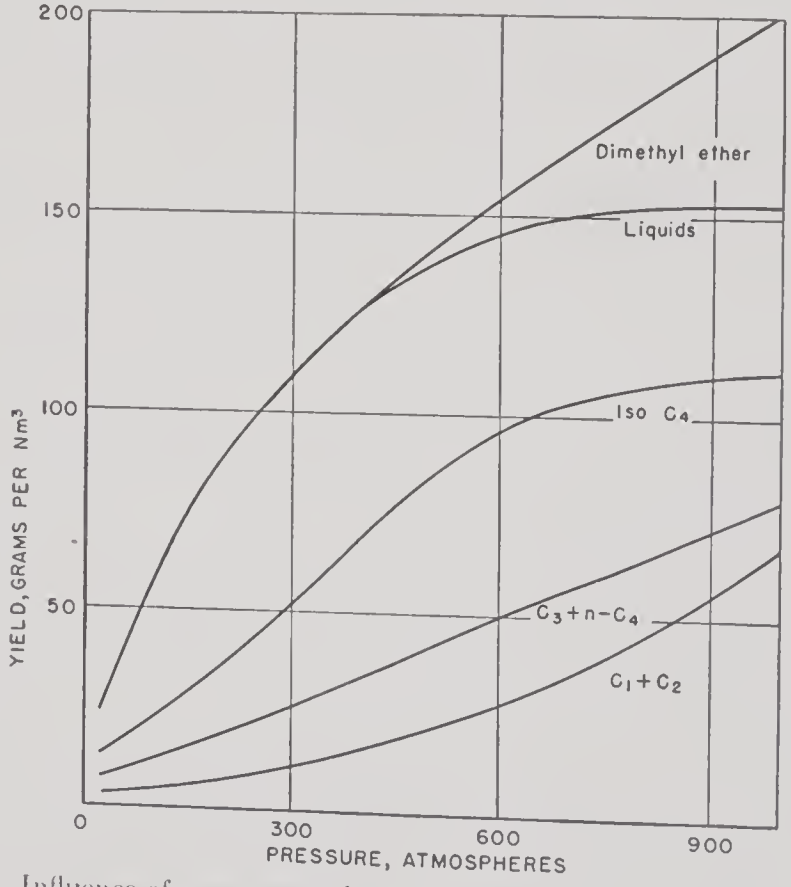


FIGURE 5–2. Influence of pressure on the amount and kind of products from the isosynthesis (ThO_2 single-component catalysts, 450°C). Reproduced from reference 27.

the effects of contact time and pressure the data shown in Table 5 were obtained. It is apparent from inspection of Table 5 that pressure increased the rate of conversion at constant contact time. Comparison of the results in the third and fifth rows of Table 5 shows that about 8 times more CO was converted at 600 atm than at 150 atm.

Table 5. Relative Effects of Contact Time and Pressure on Conversion at Constant Temperature (450°C), Using Standard Thoria Catalyst

Pressure, atm	Liters of End Gas per Hour	Contraction, per cent	Liters of Feed Gas per Hour	Average Relative Contact Time	CO Conversion, per cent
150	10	25	13.4	1.0	46
150	5	28	6.95	1.96	53
150	2.5	30	3.57	3.85	58
300	10	37	15.9	1.74	65
600	10	51	20.4	2.87	83

TWO-STAGE OPERATION AT 150 ATM, 450°C WITH PRODUCT CONDENSATION BETWEEN STAGES, USING STANDARD THORIA CATALYST

Data for a two-stage operation are contained in Table 6. Two laboratory reactors were operated separately under the conditions shown in the first two rows of Table 6 until a steady state persisted for some time.

Table 6. Two-Stage Operation with Product Condensation between Stages, 150 atm Pressure of $1CO + 1.13H_2$ Gas, 450°C, Standard Thoria Catalyst

Reactor Number	Feed Gas, l per 28 g ThO_2 per hr	Contraction, per cent	CO Conversion, per cent	$CO:H_2$, use ratio	Grams per Cubic Meter of Feed Gas			Weight Per Cent of Total Oil + Gas			
					CO_2	H_2O	Hydrocarbons	Oil	*i*-C_4	$C_3 + n$-C_4	$C_1 + C_2$
1	11.4	28	55	1.29	206	24.6	72.9	45.2	25.8	14.5	14.5
2	13.7	27	50	1.20	194	21.0	67.9	49.8	27.8	11.2	11.2
1 + 2	6.0	45	75	1.05	265	44.0	111.3	35.6	32.4	14.8	17.2
Single stage Row 2, Table 5	6.95	28	53	....	...	....	.....	....	....	....	....

Then the two reactors were connected in series through a refrigerated (−25°C) liquid-gas separator under 150 atm pressure, between the two reactors. The feed-gas rate to reactor I was kept the same as in single-

stage operation, whereas that to reactor II was replaced by the off gas from reactor I plus the cold separator. The space velocity of the two-stage operation was close to that of the single-stage operation shown in the second row of Table 5, and comparison of these data with those for the two-stage operation of Table 6 shows that such operation resulted in an increase in CO conversion from 53 to 75 per cent.

Another two-stage experiment at 150 atm was made in which the feed gas contained 48.6 per cent CO and 41.7 per cent H_2, and the temperatures of the first and second stages were different, *ie*, 430°C and 470°C, respectively. The space velocity was the same as the two-stage operation of Table 6. A hydrocarbon yield of 125.7 g per cu m of feed gas was obtained; 37.6 per cent of this was oil, and 26.8 per cent was isobutane.

RECYCLE OF 6 VOLUMES OF END GAS PER VOLUME OF FRESH GAS AT 30 ATM AND 475°C, USING THE STANDARD THORIA CATALYST

In a test of the effect of recycling end gas, this exit gas from the reactor was passed through a refrigerated liquid-gas separator under 30 atm pressure in each cycle. Tail gas was purged at the rate necessary to maintain the 30 atm pressure at the fresh feed-gas rate given in Table 7. The change in the use ratio when recycling was employed was large

Table 7. Recycle of 6 Volumes of End Gas Per Volume of Fresh Gas (43.3 Per Cent CO, 48.0 Per Cent H_2) at 30 atm, 475°C, Using Standard Thoria Catalyst

Recycle	Feed Gas, l per 28 g ThO_2 per hr	Contraction, per cent	CO Conversion, per cent	CO:H_2, use ratio	Grams per Cubic Meter of Feed Gas			Weight Per Cent of Total Oil + Gas			
					CO_2	H_2O	Hydrocarbons	Oil	*i*-C_4	C_3 + *n*-C_4	$C_1 + C_2$
None	11.4	20.5	40.0	1.14	162	17.8	51.9	22.0	18.3	25.1	34.6
6.1	12.4	29.0	32.4	0.67	73	67.4	52.6	35.8	26.2	19.1	18.8

and in the direction of increasing water production and decreasing carbon dioxide production. The yield of oil was about the same with and without recycle, but much less methane and ethane were produced in the recycle operation.

ANALYSIS OF PRODUCTS FROM ThO_2-Al_2O_3 CATALYST

The products from the iso synthesis conducted at 300 atm and 475°C were quantitatively analyzed. The catalyst was thoria containing 20 per cent alumina, prepared by separate precipitation and mixing of the washed precipitates before drying and heating to 300°C. The tubular reaction vessel contained 684 g of this catalyst. An aluminum-block furnace surrounding the tube was maintained at 425°C. The catalyst temperature in all laboratory experiments described above (pp 456–461) was close to that of the aluminum block. In this test with a much larger mass of catalyst, the temperature of the catalyst was estimated to be about 475°C. Water gas was passed through at a rate such that 205 l of end gas per hr was obtained. The contraction during a 13-day period was 42–38 per cent; the CO and H_2 conversions were, respectively, 82–70 per cent and 74–65 per cent. The product distribution was as shown in Table 8.

TABLE 8. PRODUCTS FROM ThO_2-Al_2O_3 AT 300 ATM AND 475°C

Constituent	Grams per Cubic Meter of Feed Gas	Per Cent of Total Product
Gasol		
Methane	19.5	14.2
Ethylene	1.0	0.7
Ethane	6.2	4.5
Propylene	1.3	1.0
Propane	5.5	4.0
i-Butene	7.8	5.7
i-Butane	60.7	44.2
n-Butene	3.5	2.5
n-Butane	6.7	4.9
Oil product		
C_5 (about 40 per cent olefins)	7.0	5.1
C_6 (about 30 per cent olefins)	4.5	3.3
C_7 (about 25 per cent olefins)	3.1	2.3
C_8 (about 40 per cent olefins and 5 per cent aromatics)	2.8	2.0
$>C_8$ (about 55 per cent olefins and 30 per cent aromatics)	4.9	3.6
Alcohols		
Methanol	2.8	2.0
Total	137.3	100.0

The oil product was hydrogenated, and the saturated sample further analyzed. The C_5 fraction was 34 per cent of the sample and consisted

of 90 per cent 2-methylbutane (isopentane) and 10 per cent *n*-pentane. The C_6 fraction was 21 per cent of the sample and consisted of 35 per cent 2-methylpentane, 16 per cent 3-methylpentane, and 49 per cent 2,3-dimethylbutane. The C_7 fraction was 10 per cent of the sample and consisted approximately of 35 per cent 2,4-dimethylpentane and 65 per cent of a mixture of 2-methylhexane, 3-methylhexane, and 2,3-dimethylpentane. The C_8 fraction was 5 per cent of the sample; no isomeric composition of this fraction was given. The sample contained also 19 per cent of naphthenes, and 11 per cent of hydrocarbons of molecular weight above C_8.

Kinetics and Reaction Mechanism of the Fischer-Tropsch Synthesis

CHAPTER

6

The kinetics and reaction mechanism of the Fischer-Tropsch synthesis will be discussed in this chapter. Although the synthesis has been studied rather intensively for the past twenty-five years, many aspects are not very thoroughly understood. The hypothesis that the synthesis proceeds through formation of an intermediate metal carbide has been popular ever since it was suggested by Fischer and Tropsch [1] in 1926. Thus, the formation, hydrogenation, and thermal decomposition of carbides are suitable subjects with which to begin this chapter. Then the kinetics of the hydrogenation of carbon monoxide to hydrocarbons will be considered. Since the mechanism of a catalytic reaction must explain the type and distribution of products as well as the kinetics of the reaction, the section on reaction mechanism is preceded by a description of the products of the synthesis.

Formation and Hydrogenation of Carbides and Free Carbon

The carbides of interest to this discussion are Ni_3C, Co_2C, Fe_3C, Fe_2C (Hägg), and Fe_2C (hexagonal). All these may be classed as unstable non-ionic (interstitial) carbides.[2] These carbides are hard to determine analytically because of the difficulty of distinguishing between carbidic carbon and free carbon or other carbonaceous material. Experimental methods are as follows:

Chemical analysis

Total carbon. This may be determined from changes in weight of the sample, by weight of products formed, or by combustion analysis of the sample.

[1] F. Fischer and H. Tropsch, *Brennstoff-Chem.*, **7**, 97 (1926).

[2] For a classification of carbides and a review of literature to 1944, see L. J. E. Hofer, *U. S. Bur. Mines Rept. Invest.* 3,770 (1944), p 20.

Determination of carbidic and free carbon

1. Selective hydrogenation. Many carbides can be hydrogenated at temperatures about 100°C lower than that required for free carbon; for example, Co_2C is rapidly hydrogenated at 200°C, while free carbon is not appreciably hydrogenated below 300°C.

2. Reaction with aqueous acid solutions. Many carbides react with acids to form methane while free carbon remains as a residue. It is uncertain how completely some carbides are converted to methane when dissolved in acids. Some carbides may decompose to form carbon as well as methane.

X-ray diffraction analysis

This method has been discussed in some detail on p 40 (Chapter 2). Phase identification and at least semi-quantitative analysis of carbide phases are possible from x-ray diffraction patterns. This method gives no direct estimation of the amount of free carbon in the quantities usually found.

Magnetic methods

Magnetic analysis of Fischer-Tropsch catalysts usually involves the identification of Curie Points of ferromagnetic phases as described on p 47 (Chapter 2); the method is particularly suitable for the study of iron catalysts. The accuracy of this method of analysis is greater than that of the x-ray diffraction method.

NICKEL CARBIDE, Ni_3C

X-ray diffraction studies have shown that nickel carbide, Ni_3C, has a hexagonal close-packed structure.[3] Ni_3C is not ferromagnetic. Bahr and Bahr [4] studied the carburization of nickel with carbon monoxide. The curves for the increase of carbon content as a function of time of carburization were of two classes: Below 270°C, the rate of carburization was large initially, and it decreased with the amount of carbon deposited, the carbon content asymptotically approaching that of Ni_3C, 6.37 per cent. Above 285°C, the rate was rapid initially, followed by a slower and relatively constant rate, and the carbon content exceeded that of Ni_3C. On hydrogenation at 180°C, the carbon in the sample carburized below 270°C was completely removed; a similar hydrogenation of a sample carburized above 285°C until the carbon exceeded 6.37 per cent removed only an amount of carbon equivalent to Ni_3C. The

[3] B. Jacobsen and A. Westgren, *Z. physik. Chem.*, **20B**, 361 (1933).
[4] H. A. Bahr and T. Bahr, *Ber.*, **61**, 2,177 (1928).

carbon of the sample carburized below 270°C was completely converted to methane when the sample was dissolved in acids. When the sample carburized above 285°C to a carbon content greater than 6.37 per cent was dissolved in acid, only carbon equivalent to Ni_3C was converted to methane, the rest of the carbon remaining as a black residue. Thus, carburization below 270°C formed only the carbide Ni_3C, while Ni_3C and free carbon were produced above 285°C. Carburization above 420°C produced large quantities of free carbon and very little carbide.

Tebboth [5] studied the decomposition of carbon monoxide on Ni, Ni-kieselguhr, Ni-ThO_2, and Ni-ThO_2-kieselguhr catalysts at 250°–450°C. At all temperatures in this range the pure nickel catalyst was quite inactive. At 250°C, the order of activity from greatest to least was Ni-ThO_2-kieselguhr, Ni-kieselguhr, Ni-ThO_2, and Ni. At this temperature the rate of total carbon deposition was high initially and then decreased to constant and somewhat lower values. With all except the pure nickel catalyst, more carbon than that equivalent to Ni_3C was deposited. At higher temperatures the reactivity of all except the pure nickel catalyst was great enough so that almost all the entering carbon monoxide reacted, and hence no significant difference could be found in the rates of carbon monoxide consumption. The percentage of carbide in the Ni-ThO_2-kieselguhr catalyst was 100 at 250°C, dropping to about 30 per cent at 450°C. Tebboth did not determine the surface areas of his catalysts, but from surface areas of similar nickel and cobalt catalysts (pp 72 and 67, Chapter 2) it may be inferred that most of the enhanced activity of the promoted and/or supported catalyst for both carbide and free-carbon formation was due to their greater surface areas. It should be noted that these catalysts carburized at a much greater rate than the samples of Bahr and Bahr.[4]

Chakravarty and Chakravarty [6] stated that traces of potassium carbonate accelerate the rate of formation of free carbon on nickel catalysts.

COBALT CARBIDE, Co_2C

Bahr and Jessen [7] studied the carburization of cobalt metal with carbon monoxide. As observed with nickel, the carburization curves were of two types, as shown in Figure 1. Below 230°C, the carbon content approached 9.24 per cent, which corresponds to the formula Co_2C. At 260°C and above, the carbon content increased rapidly initially; after about 6 per cent carbon had been deposited, it increased at a con-

[5] J. A. Tebboth, *J. Soc. Chem. Ind. (London)*, **67**, 62 (1948).
[6] K. M. Chakravarty and P. B. Chakravarty, *Science and Culture*, **12**, 110 (1946).
[7] H. A. Bahr and V. Jessen, *Ber.*, **63B**, 2,226 (1930).

stant rate. Hydrogenation at 250°–300°C of a sample carburized at 250°C removed almost all the carbon. Carburization at 260°C and above, if continued sufficiently long, deposited more than 9.24 per cent carbon, and hydrogenation at 250°–300°C removed only 9.0 per cent or

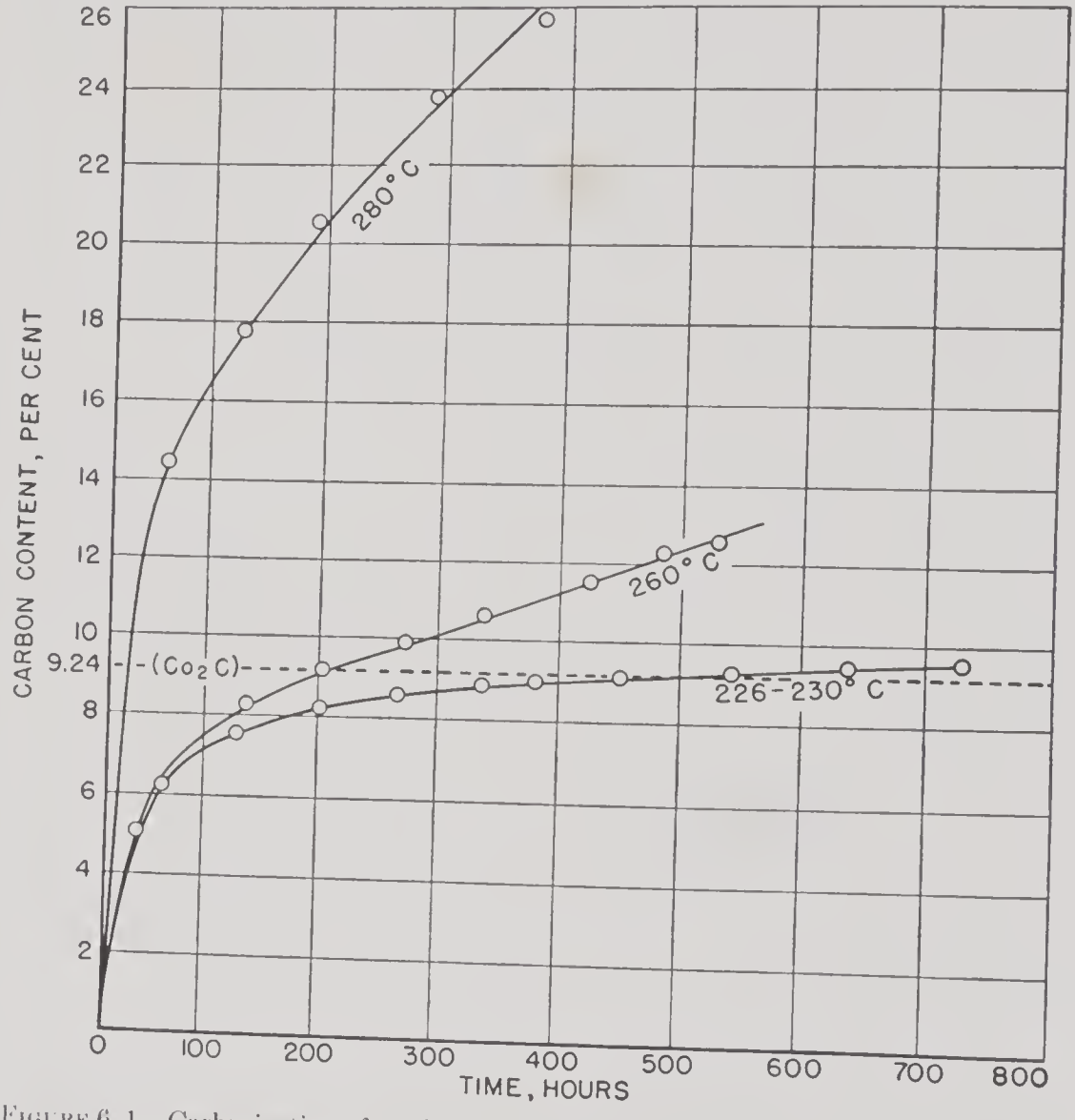


FIGURE 6–1. Carburization of a cobalt metal powder with carbon monoxide. Reproduced from reference 7.

less carbon, the amount of carbon removable by hydrogenation decreasing with increasing carburization temperature. Thus, the carbon removable by hydrogen below 300°C was assumed to be chiefly carbidic carbon. The remainder of the carbon (presumably free carbon) could be hydrogenated above 332°C.

A number of samples were carburized in two stages as shown in Table 1. In the first stage the samples were carburized at 225°C until varying

amounts of carbidic carbon had been deposited. In the second stage the samples were carburized at temperatures above 250°C until they contained considerably more carbon than that corresponding to Co_2C. Then the samples were hydrogenated at 245°C to determine the amount of carbidic carbon present. When the temperature of the second carburization was 300°C or lower, about 9.0 per cent carbon was removed

Table 1. Two-Stage Carburization of Cobalt [a]

Sample	First Carbon Monoxide Treatment			Second Carbon Monoxide Treatment			Carbon Removed by Hydrogenation		
	Temperature, °C	Time, hr	Carbon, per cent	Temperature, °C	Time, hr	Total Carbon, per cent [b]	Temperature, °C	Carbon, per cent	
								From Weight Loss	From Methane Determination
31M	225	606	7.73	250–258	200	9.13	244	8.92	9.00
51B	226	45	3.17	280	64	20.7	243	7.83	8.38
38B	225	140	7.38	283	133	16.25	246	9.12	9.28
40B	226.5	47	5.59	294	46	14.85	244	8.80	9.03
55B	225	203	7.92	300	45	16.52	243.5	8.82	9.33
39B	227	936	8.12	315.5	45	34.96	246.5	0.36	0.23
60B	227	276	~9	328	43	~51.7	245	0.32	0.29
41B	226	381	7.87	520	10–20	37.0	245.5	0.2	0.2

[a] H. A. Bahr and V. Jessen; see reference 7.
[b] Total carbon present in the sample after the first and second carbon monoxide treatments.

by hydrogenation, but when the temperature of the second carburization was above 300°C, the carbon removed by hydrogenation was only 0.2–0.3 per cent. Thus, above 300°C, the thermal decomposition of cobalt carbide must be more rapid than carbide formation.

Hofer and Peebles [8] presented the x-ray diffraction pattern of Co_2C prepared by carburizing a cobalt metal powder. Their gravimetric data (Table 2) are in general agreement with those of Bahr and Jessen.[7] The carbide, Co_2C, had an x-ray diffraction pattern that was distinct from that of either α- or β-cobalt. This carbide pattern, which was observed in all samples carburized below 290°C, disappeared on hydrogenation.

Hofer and Peebles [9] made x-ray diffraction studies of carburized cobalt catalysts having the following composition: Catalyst 108B, Co:ThO_2:kieselguhr = 100:18:100; and catalyst 89K, Co:ThO_2:MgO:kieselguhr = 100:6:12:200. The raw catalysts were reduced in hy-

[8] L. J. E. Hofer and W. C. Peebles, *J. Am. Chem. Soc.*, **69**, 895 (1947).
[9] L. J. E. Hofer and W. C. Peebles, *ibid.*, **69**, 2,497 (1947).

TABLE 2. X-RAY STUDIES OF CARBURIZED AND HYDROGENATED COBALT [a]

Experiment	Carburization			Hydrogenation			X-ray Diffraction Analysis
	Temperature, °C	Time, hr	Total Carbon, per cent	Temperature, °C	Time, hr	Carbidic Carbon, per cent	
11	Original reduced sample						α-Co
	218	136	2.77				α-Co, Co_2C
	218	1,634	9.07 [b]				Co_2C
	218	1,634	9.13 [b]	218	149	8.50	α-Co
17	Original reduced sample						α-Co
	243	93	6.29				α-Co, Co_2C
	243	448	10.69 [b]				Co_2C
	243	448	9.14 [b]	243	93	3.94	α-Co
18	266	20	5.33				α-Co
	266	64	16.92				α-Co, Co_2C
	266	341	39.27 [b]				α-Co, Co_2C, C
	266	341	41.02 [b]	266	44	7.72	α-Co, C
16	Original reduced sample						α-Co
	292	47	5.33				α-Co
	292	112	36.51				α-Co, C
	292	205	60.21				α-Co, Co_3O_4, C
19	390	7.8	21.0				α-Co
	390	12.7	32.64				α-Co, C
	390	24.3	46.39 [b]				α-Co, C
	390	24.3	47.27 [b]	292	31.4	0.00	α-Co, C

[a] L. J. E. Hofer and W. C. Peebles; see reference 8.

[b] In each experiment four tubes of cobalt oxide were reduced at the same time and under identical conditions. One tube was removed for x-ray analysis and the other three were carburized. After each stage of carburization or hydrogenation, one of the tubes was removed for x-ray analysis. This accounts for the slight differences in per cent carbon that are observed.

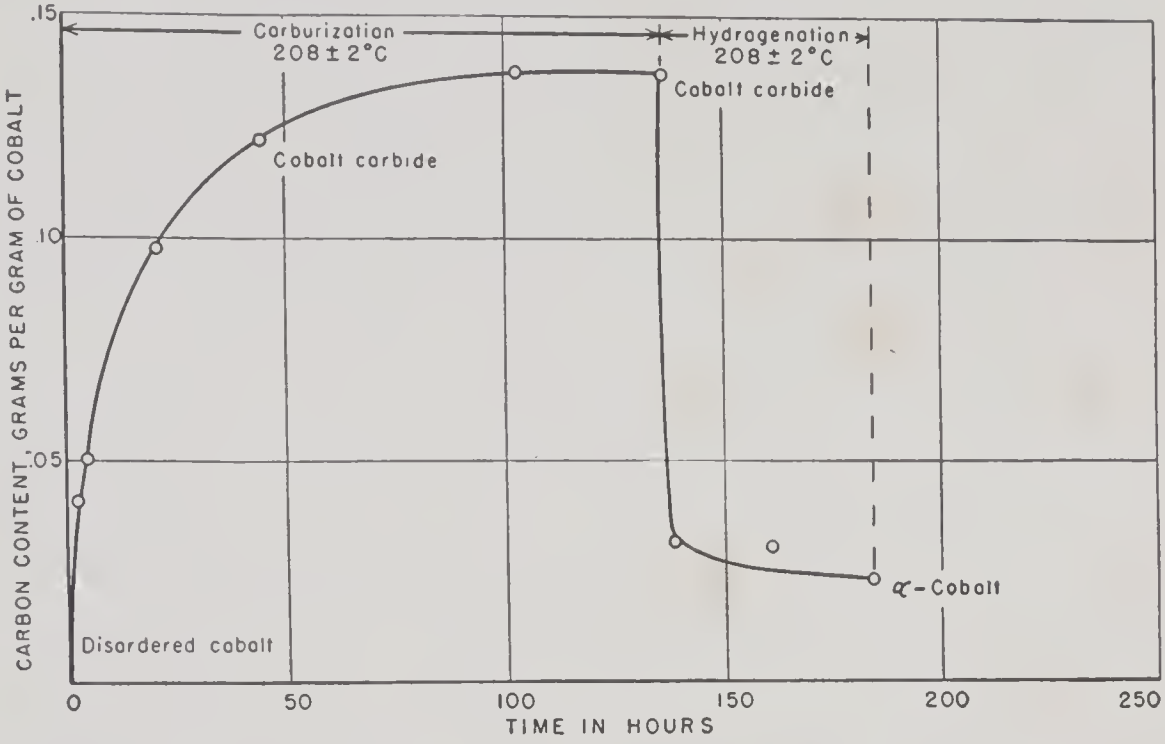


FIGURE 6–2. Carburization of cobalt-thoria-magnesia-kieselguhr catalyst 89K with carbon monoxide and its subsequent hydrogenation at 210°C. Reproduced by permission from reference 9.

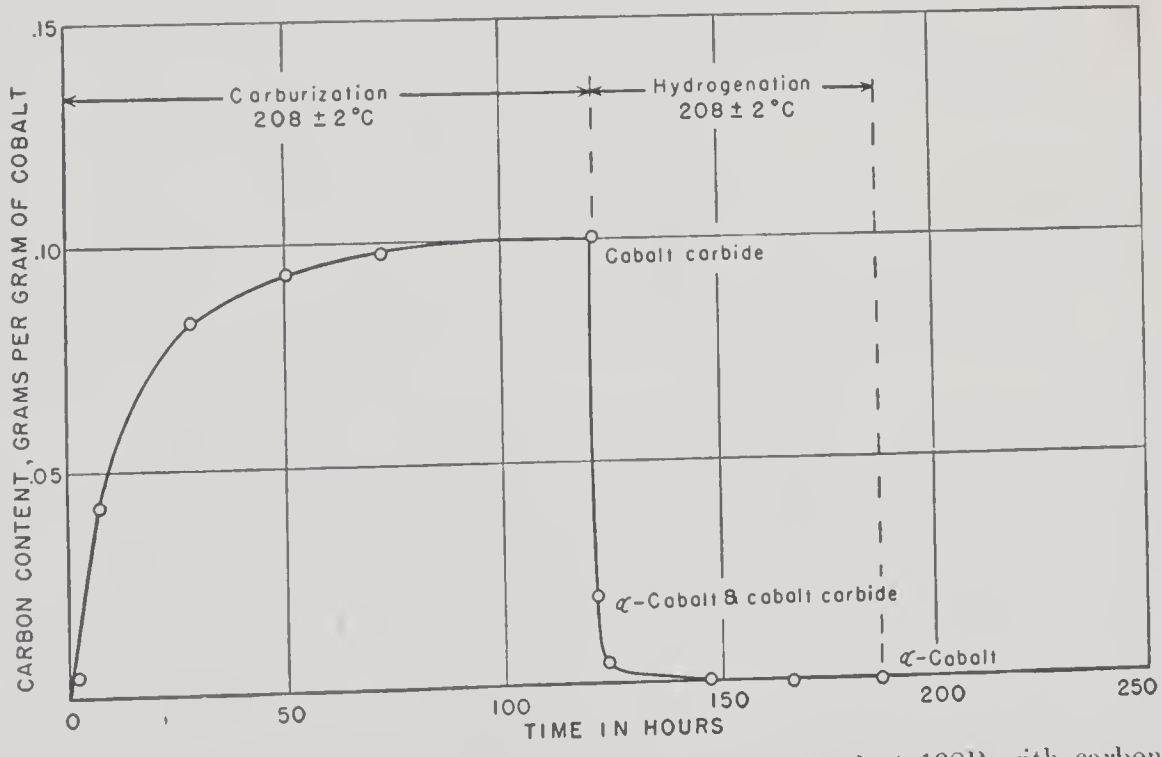


FIGURE 6–3. Carburization of cobalt-thoria-kieselguhr catalyst 108B with carbon monoxide and its subsequent hydrogenation. Reproduced by permission from reference 9.

drogen at 400°C, carburized in carbon monoxide at 208°C, and hydrogenated at 208°C. The catalyst composition was determined at each stage by x-ray diffraction analysis and change in weight. In Figures 2 and 3 are shown carbon content-time curves for carburization and hydrogenation of catalysts 89K and 108B. The carbon:cobalt ratio of catalyst 108B closely approached that of Co_2C (0.1015), while the carbon:cobalt ratio of 89K approached 0.137.

The reduced catalyst gave diffuse x-ray diffraction patterns of disordered layer structure cobalt, and after carburization, the pattern of

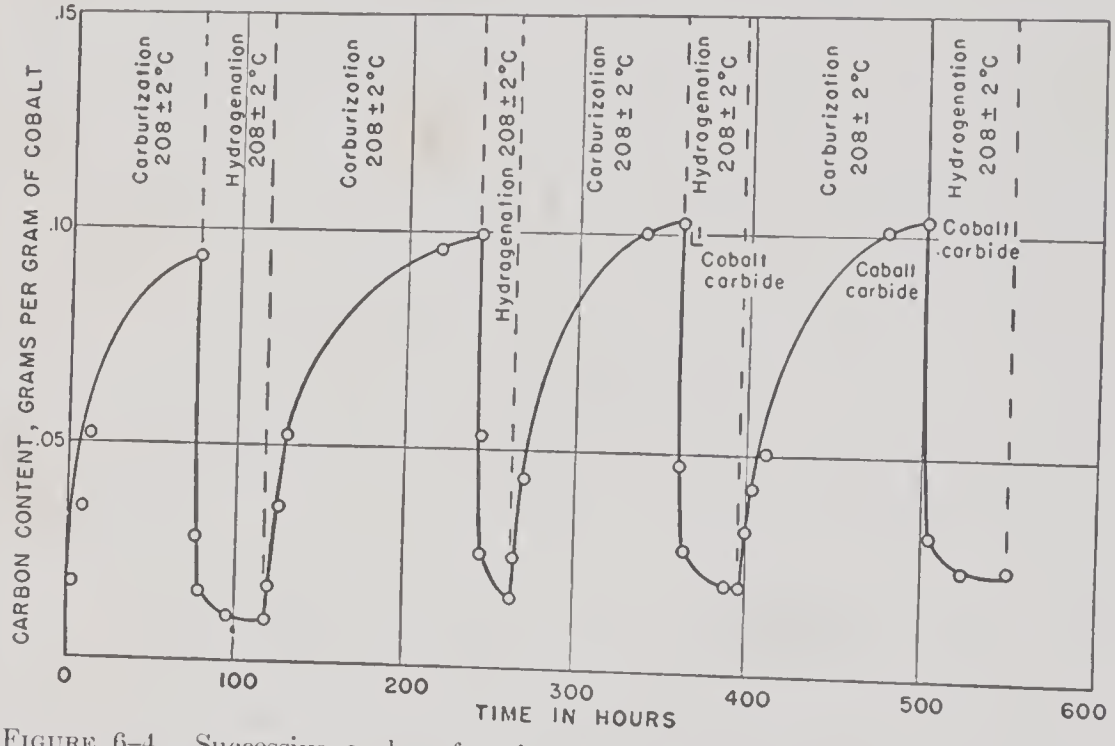


FIGURE 6–4. Successive cycles of carburization and hydrogenation of a cobalt-thoria-kieselguhr catalyst 108B at 210°C. Reproduced by permission from reference 9.

Co_2C. After hydrogenation of the carbide, the pattern of α-cobalt was observed. The metastable disordered cobalt was converted to stable α-cobalt by the formation and hydrogenation of Co_2C. The rate of hydrogenation of the carbide was very rapid, and carbon equivalent to Co_2C was removed. With catalyst 89K, some of the carbon was not removed by hydrogenation at 208°C; this was equal to the carbon in excess of Co_2C, and was presumably free carbon. The cycle of carburization-hydrogenation can be repeated many times without any major change in the rate or extent of carburization, as shown in Figure 4. The amount of free carbon increased somewhat with each cycle.

The rates of carburization of these catalysts were about 10 times greater than that of the cobalt metal powder. This is not unexpected,

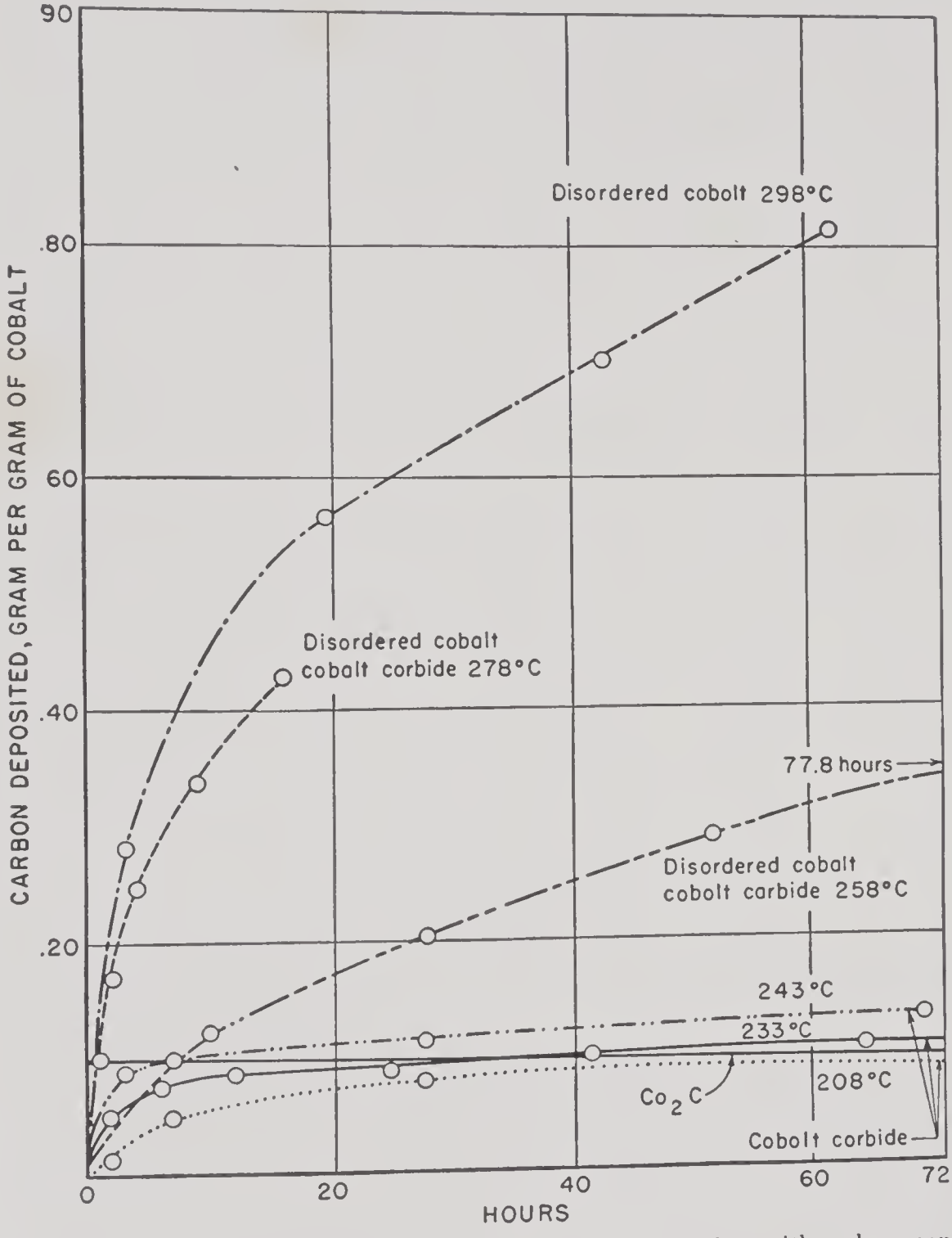


FIGURE 6–5. Carburization of a cobalt-thoria-kieselguhr catalyst with carbon monoxide in the temperature range 208°–298°C. Reproduced by permission from reference 11.

since the surface areas of the reduced catalysts 108B and 89K were 32.4 and 62.7 sq m per g, respectively, as compared with 3.2 sq m per g for the cobalt metal powder.[10]

Data of Hofer, Peebles, and Bean [11] in Figure 5 illustrate the two types of carburization curves for cobalt catalysts. Below 243°C the weight ratio of carbon to cobalt approached as a limit a value equal to or slightly greater than that of Co_2C, and these samples gave the x-ray diffraction pattern of Co_2C. Above 243°C, the curves increased approximately linearly after 20 hr, and the final carbon:cobalt ratio was as much as 8 times the value equivalent to Co_2C. The samples carburized at 258° and 278°C gave x-ray diffraction patterns of disordered cobalt and cobalt carbide, and the sample carburized at 298°C gave the pattern of disordered cobalt but no carbide pattern. Table 3 presents

Table 3. Carbon Deposition on Cobalt-Thoria-Kieselguhr Catalyst [a]

(Catalyst reduced at 400°C in H_2.)

Carbon Monoxide Treatment		Carbon:Cobalt Ratio		
Temperature, °C	Time, hr	Total Carbon	Carbidic Carbon [b]	Recarbided Carbon [c]
298	62	0.820	0.017	0.008
278	15	0.435	0.054	.....
258	78	0.352	0.063	0.089
243	71	0.138	.....	....
233	112	0.120	0.099	....
208	121	0.104	0.104	0.99

[a] L. J. E. Hofer, W. C. Peebles, and E. H. Bean; see reference 11.

[b] Amount of carbon that was removed by hydrogenation at temperature of carbon deposition.

[c] Amount of carbidic carbon that could be added by carbon monoxide treatment at 220°C.

the total and carbidic carbon content of the samples after the carburizations shown in Figure 5, carbidic carbon being determined by hydrogenation at the temperature of the carburization. These data substantiate the x-ray analyses of the carburized catalysts. Three of

[10] See Table 5 of Chapter 2.

[11] L. J. E. Hofer, W. C. Peebles, and E. H. Bean, *J. Am. Chem. Soc.*, **72**, 2698 (1950).

the samples were recarbided at 220°C, after the hydrogenation. The samples that were initially carburized at 258°C and below gained an amount of carbon equivalent to Co_2C, but the sample initially carburized at 298°C gained less than 10 per cent of the carbon equivalent to Co_2C. Thus, carburization at 298°C poisoned the catalyst for subsequent carbide formation at 220°C.

To check the validity of the hydrogenation method of analyzing for carbidic carbon, Hofer, Peebles, and Bean [11] studied the hydrogenation of a carburized cobalt-thoria-kieselguhr catalyst. The reduced catalyst was carburized with carbon monoxide for 122 hr at 258°C to a carbon:cobalt ratio of 0.2554 and was then hydrogenated at 180°C until there was no further weight loss (111 hr). Carbon equal to a carbon:cobalt ratio of 0.0841 was removed. After this treatment the sample was hydrogenated at 210°C to constant weight, and in a similar manner at successively higher temperatures, as shown in Figure 6, the length of each hydrogenation varying from 45 to 159 hr. After 115 hr at 400°C, carbon corresponding to a carbon:cobalt ratio of 0.0086 remained. Below 210°C, carbon approximately equivalent to Co_2C was removed. Then, no sizable amount of carbon was removed until 270°C. The amount of carbon removed increased to a maximum at 360°C, and 96 per cent of the carbon had been removed by 400°C. This demonstrates that the hydrogenation analysis is satisfactory for cobalt catalysts: carbidic carbon is removed below 210°C and free carbon at 270°C and above.

Hofer, Cohn, and Peebles [12] studied the isothermal decomposition of cobalt carbide in carburized catalyst 108B by a magnetic method. The catalyst was reduced completely and carburized to greater than 90 per cent. In the decomposition, non-ferromagnetic Co_2C with a small magnetic moment is converted to ferromagnetic cobalt metal with a high magnetic moment, and the observed magnetic moment is proportional to the extent of decomposition of the carbide. The thermal decomposition occurred with the sample in place in the magnetic balance. As shown in Figure 7, the carbide decomposed slowly at 300°C, and the rate increased to a great extent with temperature. In the range 80–25 per cent cobalt carbide, the decomposition-time curves were linear, the reaction being of apparent zero order. An apparent overall activation energy of 54.3 kcal per mole was computed for this zero order range.

Anderson, Hall, Krieg, and Seligman [13] studied the effect of carburization and hydrogenation on the surface area of cobalt-thoria-

[12] L. J. E. Hofer, E. M. Cohn, and W. C. Peebles, *J. Phys. & Colloid Chem.*, **53**, 661 (1949).

[13] R. B. Anderson, W. K. Hall, A. Krieg, and B. Seligman, *J. Am. Chem. Soc.*, **71**, 183 (1949).

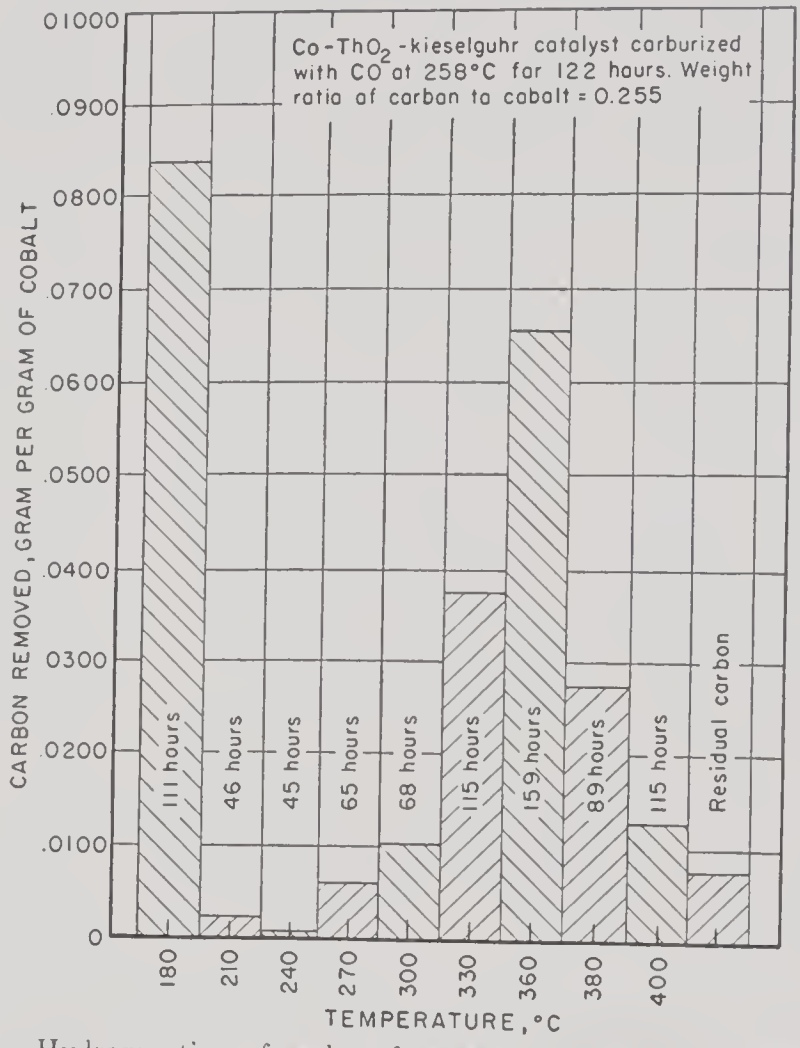


FIGURE 6–6. Hydrogenation of carbon from a carburized cobalt catalyst at increasing temperatures. Sample hydrogenated to constant weight at each temperature. Reproduced by permission from reference 11.

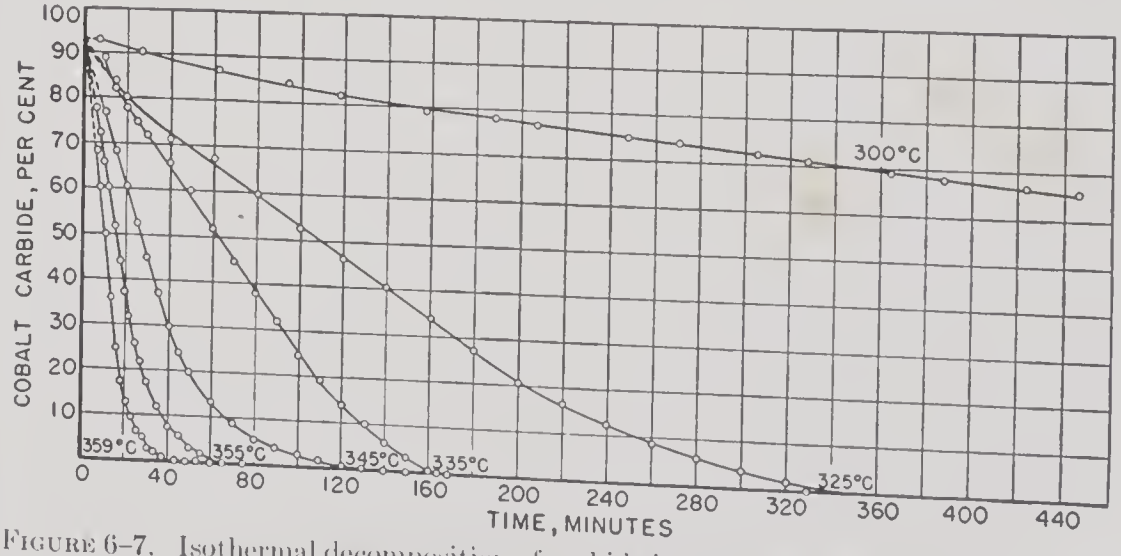


FIGURE 6–7. Isothermal decomposition of carbide in carbided cobalt Fischer-Tropsch catalyst. Reproduced by permission from reference 12.

kieselguhr catalyst 108B, as summarized in Table 4. Carburization and hydrogenation at 208° and 235°C did not change the total area significantly. The fraction of cobalt in the surface of the carburized catalysts (1-C and 2-C), as indicated by chemisorption of carbon monoxide

TABLE 4. EFFECT OF CARBURIZATION AND HYDROGENATION ON THE SURFACE AREA OF COBALT CATALYST 108B [a]

(All data per gram of unreduced catalyst.)

Number	Treatment				Weight Change on Treatment, mg per g	Per Cent Carbon, Based on Co_2C	Surface Area, sq m per g	V_m,[c] cc per g	V_{CO},[d] cc per g	$\frac{V_{CO}}{V_m}$
	SVH [b]	Gas	Temperature, °C	Time, hr						
	Original catalyst				.....	.....	71.6	16.3	0.0	.....
1-R	3,000	H_2	360	2.0	−230.0	0.0	32.6	7.44	3.00	0.403
1-C	100	CO	208	15.5	+ 34.4	112.0	31.5	7.18	0.94	0.131
2-R	100	H_2	208	16.0	− 34.7	6.1	30.1	6.88	1.44	0.209
2-C	100	CO	235	12.5	+ 32.9	114.5	....	....	....	.....
				59.5	+ 5.1	130.1	32.0	7.32	0.78	0.107
3-R	100	H_2	208 [e]	12.5	− 33.4	30.5	31.2	7.12	....	.....
				30.7	− 0.4	29.3	31.3	7.14	0.85	0.119
3-C	100	CO	275	16.0	+127.4	418.2	50.6	11.54	1.30	0.113
4-R	100	H_2	208	18.0	− 7.1	398.0	50.0	11.40	1.29	0.113
4-C	100	CO	208	16.0	+ 8.1	423.5	50.8	11.59	1.05	0.091
5-R	3,000	H_2	360	2.0	− 35.3	319.0	51.4	11.74	1.30	0.111
5-C	100	CO	208	17.3	+ 10.6	354.8	52.2	11.92	....	.....
6-R	3,000	H_2	360	22.0	− 45.1	216.5	....	.....	....	.....
				64.0	− 19.8	156.1	46.8	10.7	1.48	0.138
				157.3	− 20.4	93.8	....	....	....	.....
				296.3 [f]	− 28.1	7.8	35.2	8.03	1.99	0.248
6-C	100	CO	208	18.0	+ 18.0	72.3	....	....	....	.....

[a] R. B. Anderson, W. K. Hall, A. Krieg, B. Seligman; see reference 13.
[b] Space velocity per hr [volumes of gas (STP) per volume of catalyst per hr].
[c] Volume of nitrogen necessary to form a monolayer.
[d] Volume of chemisorbed carbon monoxide at −195°C.
[e] Temperature controller failed and temperature rose to 250°C for a short period.
[f] Temperature controller failed and temperature rose to 450°C in part of this period.

at −195°C, was less than half as much as on the hydrogenated catalysts (1-R and 2-R). On reduction (2-R) the amount of chemisorbed carbon monoxide increased but was still less than 1-R. Carburization at 275°C, which deposited 4 times as much carbon as that in Co_2C, increased the surface area considerably. Most of the gain in weight was free carbon, since only a small fraction was removable by hydrogenation (4-R). Carburization (4-R) at 208°C indicated that the catalyst was "poisoned" for the formation of carbide, as also observed by Hofer,

Peebles, and Bean.[11] Reduction (6-R) at 360°C removed nearly all the carbon and decreased the surface area to nearly that of the original reduced catalyst. Reduced catalyst (6-R) chemisorbed more than twice as much carbon monoxide as after reduction (5-R), but still less than 1-R. The remaining carbon, equivalent to 7.8 per cent Co_2C, prevented the catalyst from being fully carbided at 208°C (6-C).

Thus carbidic carbon does not change the total surface area but decreases the amount of carbon monoxide chemisorbed at −190°C. Free carbon increases the total area considerably and decreases the amount of chemisorbed carbon monoxide. Free carbon inhibits the formation of carbide.

CARBIDES OF IRON

Bahr and Jessen [14] studied the carburization of both iron and iron oxide with carbon monoxide. With cobalt and nickel there is no tendency to oxidize the metal in carburization with carbon monoxide, but with iron some oxide is usually found whether the starting material is metal or oxide. The carburized catalysts were analyzed by hydrogen treatment and determination of the amounts of methane and water produced. Samples of iron oxide that were treated with carbon monoxide for more than 400 hr were reduced and carburized to a considerable extent and contained 23–32 per cent carbon and about 3.5 per cent oxide. Hydrogenation at 257°C removed 9.2 and 9.5 per cent carbon, approximately the equivalent of Fe_2C.

Samples of iron oxide were completely reduced in hydrogen at 290°C, carburized with carbon monoxide at various temperatures, and analyzed by hydrogenation as shown in Table 5. The iron was not oxidized at carburization temperatures less than 330°C. Oxidation can occur if the carbon dioxide:carbon monoxide ratio exceeds the equilibrium constant for the oxidation of iron with carbon dioxide (Table 17, Chapter 1). The carbon removable by hydrogenation at 290°C of the samples of Table 5 varied from 7.1 to 8.2, less carbon than that in Fe_2C but more than Fe_3C. Almost all the carbon was removed by hydrogenation at 450°C. The authors stated that iron oxide reduced at 247° and 262°C can be carburized to an amount equivalent to Fe_2C in 200–300 hr at 225°C. Thus, these data indicate the formation of a carbide approximating the composition Fe_2C, but the evidence is not conclusive.

Hofmann and Groll [15] carburized iron oxide with carbon monoxide at 275° and 320°C. The x-ray diffraction pattern of these samples contained lines of magnetite, of cementite, and of a substance obtained by

[14] H. A. Bahr and V. Jessen, *Ber.*, **66B**, 1,238 (1933).

[15] U. Hofmann and E. Groll, *Z. anorg. u. allgem. Chem.*, **191**, 414 (1930).

Brill and Mark [16] by thermal decomposition of $Fe(CN)_2$. This led Bahr and Jessen [14] to postulate that their samples carburized above 240°C contained Fe_3C as well as Fe_2C. Material having approximately the

Table 5. Formation and Hydrogenation of Carbide in Reduced Iron [a]

Reduction		Carbon Monoxide Treatment				Analysis, per cent					Residual Carbon, mg
						Iron as Fe_3O_4 from			Carbon from		
Time, hr	Temperature, °C	Time, hr	Temperature, °C	l per g	Composition, g	Weight Loss Minus Carbon	Water	Temperature, °C	Methane	Weight Loss Minus Oxygen	
497	292	994	240	0.8	1.4235 Fe 0.1440 C	0		291 322 446	7.43 7.62 9.12		5.6
486	290	350	273	0.8	1.5181 Fe 0.1993 C	0		291 318 401	7.75 7.92 11.66		4.1
190	290	65	324	0.8	0.9950 Fe 0.2288 C	0		291 322 446	7.65 8.08 19.44		0.4
200	291	93	333	0.5 1.5	1.5682 Fe 0.6338 C + O	4.45	2.04	287 316 483	8.23 8.23 29.0	8.02 8.10 29.0	5.5
143	291	1.6	354	1.5	1.458 Fe 0.1234 C + O	0.68	1.22	280 317 483	7.12 7.12 8.05	7.07 7.15 7.92	0.9
206	290	441	362	0.8	1.8080 Fe 1.1017 C + O	7.36	7.39	291 322 450	7.75 7.72 38.7	7.40 38.7	3.1

[a] H. A. Bahr and V. Jessen; see reference 14.

composition of Fe_2C but a different x-ray diffraction pattern was obtained by Hägg [17] from carburization of reduced iron with carbon monoxide at 225°C and by Jack [18] from the action of carbon monoxide on iron nitride.

[16] R. Brill and H. Mark, *Z. physik. Chem.*, **133**, 443 (1928).

[17] G. Hägg, *Z. Krist.*, **89**, 92 (1934).

[18] K. H. Jack, *Nature*, **158**, 60 (1946); *Proc. Royal Soc. (London)*, **195A**, 34, 41, and 56 (1948).

Captured German documents contain reports of Herbst and Halle [19] and Pichler and Merkel [20] describing studies of the iron carbides of formula Fe_2C. However, these data were difficult to compare since the former investigators studied the carbides by x-ray diffraction and the latter by magnetic methods. Hofer, Cohn, and Peebles [21] studied the Fe_2C carbides with both x-ray and magnetic methods and have shown that there are two Fe_2C carbides. The first, presumably the hexagonal carbide of Herbst and Halle,[19] is the same as that of Hofmann and Groll [15] and has a Curie Point of 380°C. The second, the Hägg carbide, is the carbide of Pichler and Merkel, with a Curie Point of 247°–265°C.

Documents from the I.G. Farben.[19] contain reports of work of Herbst, Halle, and Brill, describing x-ray studies of used iron Fischer-Tropsch catalysts. These reports state that x-ray diffraction lines of the hexagonal carbide were always found in inducted or used precipitated Fe-Cu-Al_2O_3-K_2O and Fe-Cu-MgO-K_2O catalysts, while similar fused and calcined copper-free catalysts gave diffraction lines of the Hägg carbide. In 1942, Herbst reported that the hexagonal carbide was found in copper-free catalysts that had been used in the synthesis at relatively low temperatures. A used Fe-Al_2O_3-CaO-K_2O catalyst presumably tested at low temperatures contained principally the hexagonal carbide and small amounts of Hägg carbide. This sample was extracted with "benzine," evacuated, and then heated to various temperatures. Heating at 275° and 290°C for 3 hr resulted in some decomposition of hexagonal carbide to Hägg carbide. The hexagonal carbide was completely transformed to Hägg carbide in 3 hr at 330°C. With catalysts containing 6–7 per cent of copper, the hexagonal carbide was noticeably decomposed at 350°–400°C and completely transformed to Hägg carbide in 3 hr at 430°–450°C. The hexagonal carbide in a catalyst containing 2.7 per cent of copper was completely transformed to Hägg carbide in 3 hr at 350°–400°C. Thus, the thermal stability of the hexagonal carbide increased with increasing amounts of copper.

The dissertation of Merkel [20] describes work directed by Pichler at the Kaiser Wilhelm Institut für Kohlenforschung. The first portion of the dissertation describes the formation of free and carbidic carbon on a catalyst prepared by precipitation from a hot solution of iron nitrate with sodium carbonate solution. The precipitate was washed,

[19] F.I.A.T. Reel R-19, Frames 7,136–47; Group Leader Conferences, Ludwighafen, T.O.M. Reel 26, Bag 2,463; Report, Dr. Wenzel, T.O.M. Reel 134, Item II/10.

[20] H. Pichler and H. Merkel, *U. S. Bur. Mines Tech. Paper* 718 (1949). This paper contains a résumé of available data on carbides of iron, including a summary by L. J. E. Hofer of the material in reference 19.

[21] L. J. E. Hofer, E. M. Cohn, and W. C. Peebles, *J. Am. Chem. Soc.*, **71**, 189 (1949).

alkalized with potassium carbonate (amount not specified but presumably at least 0.1 part per 100 of iron), and oven-dried at 105°C. The catalyst was carburized in an aluminum-block furnace and transferred by a suitable technique to an apparatus in which the sample was decomposed in 5 *N* hydrochloric acid solution. The gases evolved in the acid decomposition were collected, measured, and analyzed. Carbidic carbon was assumed to form gaseous hydrocarbons. The insoluble residue which contained only small amounts of iron was analyzed, and its carbon content assumed to be free carbon. One of the objectives of this study was to demonstrate why pretreatment of this type of catalyst with pure carbon monoxide at 325°C and 0.1 atm gave catalysts of maximum activity, as shown by catalyst-testing experiments. Most of the experiments centered about these conditions of carburization.

The effect of pressure on the carburization of alkalized iron catalysts at 325°C is shown in Table 6. These data indicate that the rate of forma-

Table 6. Effect of Pressure on the Carburization of Alkalized Iron Oxide Catalysts at 325°C [a]

(25 hr of treatment with carbon monoxide at 4 l per 10 g Fe per hr.)

Pressure, atm	Grams Carbon per 10 g Fe	
	Free Carbon	Carbide
0.1	2.21	0.45
1.0	4.23	0.34
15.0	Not determined	0.10

[a] H. Pichler and H. Merkel; see reference 20.

tion of carbide varied inversely with pressure, whereas free-carbon formation varied directly with pressure. Table 7 contains data on the formation of free and carbidic carbon as a function of carburization temperature. The formation of free carbon increased with temperature, be-

Table 7. Effect of Temperature on Carburization of an Alkalized Iron Oxide Catalyst [a]

(25 hr of treatment with carbon monoxide at 4 l per 10 g Fe per hr.)

Temperature, °C	Grams Carbon per 10 g Fe	
	Free Carbon	Carbide
175	0.00	0.003
225	0.07	0.004
275	0.89	0.358
325	2.21	0.454
425	10.02	0.017

[a] H. Pichler and H. Merkel; see reference 20.

coming sizable at 325°C and above, whereas the formation of carbidic carbon increased to a maximum at 325°C.

The formation of free and carbidic carbon and the oxygen content of an alkalized iron oxide catalyst as a function of time are shown in Figure 8. After 3 hr, the amount of carbidic carbon had increased to

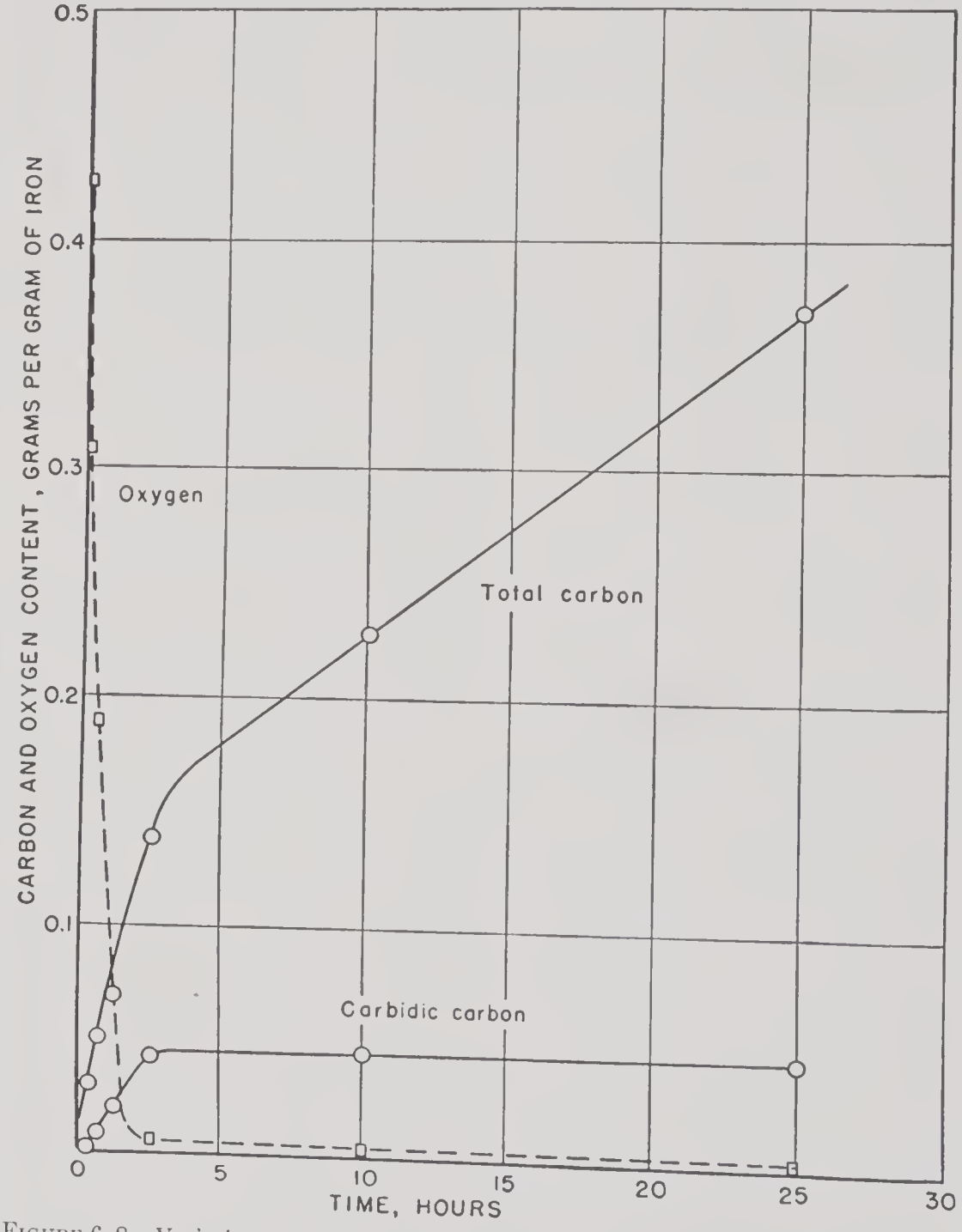


FIGURE 6-8. Variation of composition of an alkalized iron catalyst during carburization with 4 l (STP) of carbon monoxide per g of iron per hr at 0.1 atm and 325°C. Reproduced from reference 20.

0.4 g carbon per 10 g iron, and it increased only slightly with additional carburization. In the first 3 hr, most of the oxygen was removed from the catalyst. After 10 hr, the amount of oxygen remaining was only 1 per cent of that in the unreduced catalyst. Probably a sufficient amount of carbon dioxide is formed by the carburization reactions to prevent further reduction of the iron oxide. The total carbon curve increased rapidly initially and then decreased to a constant rate at about the point where the carbide content became constant. Under these conditions the amounts of carbide and oxygen did not change after 3 hr.

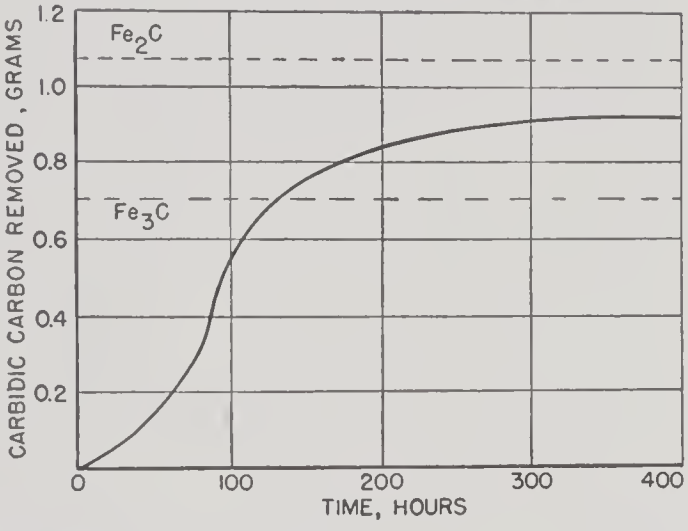


FIGURE 6–9. Hydrogenation of 10.060 g of a carburized, alkali-promoted (0.25% K_2CO_3) catalyst at 263°C and atmospheric pressure, 0.8 l of hydrogen per hr. Reproduced from reference 20.

The results of analysis by the acid decomposition method indicated that the carbidic carbon was equivalent to only 50 per cent of that in Fe_2C, and that hydrogen was formed in excess of the calculated amount. It is probable that some carbidic carbon appeared as free carbon; however, this does not seriously alter the interpretation of Figure 8. To check this point, a sample of alkalized iron oxide catalyst was carburized with 40 l of carbon monoxide per hr per 10 g of iron for 8 hr (presumably at 325°C and 0.1 atm) to insure complete carburization. This sample was hydrogenated at 263°C for long periods and the methane produced was determined; these data are given in Figure 9. This temperature was considered optimum for removal of carbide without hydrogenation of free carbon. The carbide removed after 400 hr of hydrogenation was equal to a value between those equivalent to the formulae, Fe_2C and Fe_3C, an amount corresponding to $Fe_{2.28}C$. This hydrogenated catalyst was subjected to acid decomposition analysis, and no carbidic carbon was found. This shows that free carbon does not appear as carbide in this analysis; however, a part of the carbide probably appeared as free carbon.

In the second part of the dissertation, Pichler and Merkel discussed thermomagnetic studies of the formation and decomposition of iron carbides. As described in Chapter 2 (p 48), thermomagnetic analysis involves the determination of Curie Points (CP), the steepest portions or points of inflection of the thermomagnetic curves. Pichler and Merkel [20] and Hofer [20,21] have listed the Curie Points of various iron phases, as shown in Table 8. Hofer [20,21] observed the Curie Point of

Table 8. Curie Points of Phases Present in Iron Fischer-Tropsch Catalysts

Phase	Curie Point, °C
α-Fe	768
Hexagonal, Fe_2C	380
Hägg, Fe_2C	247–265
Cementite, Fe_3C	210
Magnetite, Fe_3O_4	565
Cubic or γ-Fe_2O_3	590 (500–675)
α-Fe_2O_3	Paramagnetic or weakly ferromagnetic
FeOOH phases	Paramagnetic
Potassium ferrite, K_2O-Fe_2O_3	150
Copper ferrite, CuO-Fe_2O_3	450

Fe_2C (Hägg) at 247°C, as compared with the value of 265°C reported by Pichler and Merkel.[20] This difference is apparently due to experimental uncertainties, for there is no reason to doubt that the Curie Points correspond to the same carbide.

Pichler and Merkel made preliminary, orienting experiments on the formation and stability of iron carbides. A Curie Point of 260°C was observed on an iron oxide-potassium carbonate catalyst carburized with carbon monoxide at 0.1 atm and 325°C. An iron oxide-copper oxide-potassium carbonate catalyst carburized at 205°C had Curie Points at 265°C and 380°C. Comparison with the data of Herbst and Halle [19] and Hofer [20,21] indicates that the CP = 260°–265°C carbide was Hägg Fe_2C and the CP = 380°C carbide was hexagonal Fe_2C. The thermal decomposition of these carbides in an $Fe:Cu:K_2CO_3$ (100:1.0:0.25) catalyst that was carburized at 205°C is presented in Figure 10. Portions of the carburized catalyst were heated for 30 min in nitrogen at several temperatures, and thermomagnetic curves determined. The 300°C heating (Figure 10*B*) changed the magnetic curve only slightly, the presence of some free iron being observed. On heating at 355°C, the amount of CP = 380°C carbide decreased considerably, it being transformed to CP = 265°C carbide. After the 400°C heating, only a small amount of CP = 380°C carbide remained; however, the amount

of CP = 265°C carbide was essentially unchanged. After the 480°C heating, the CP = 380°C disappeared, and the amount of free iron increased. A Curie Point was observed at about 230°C. Apparently this

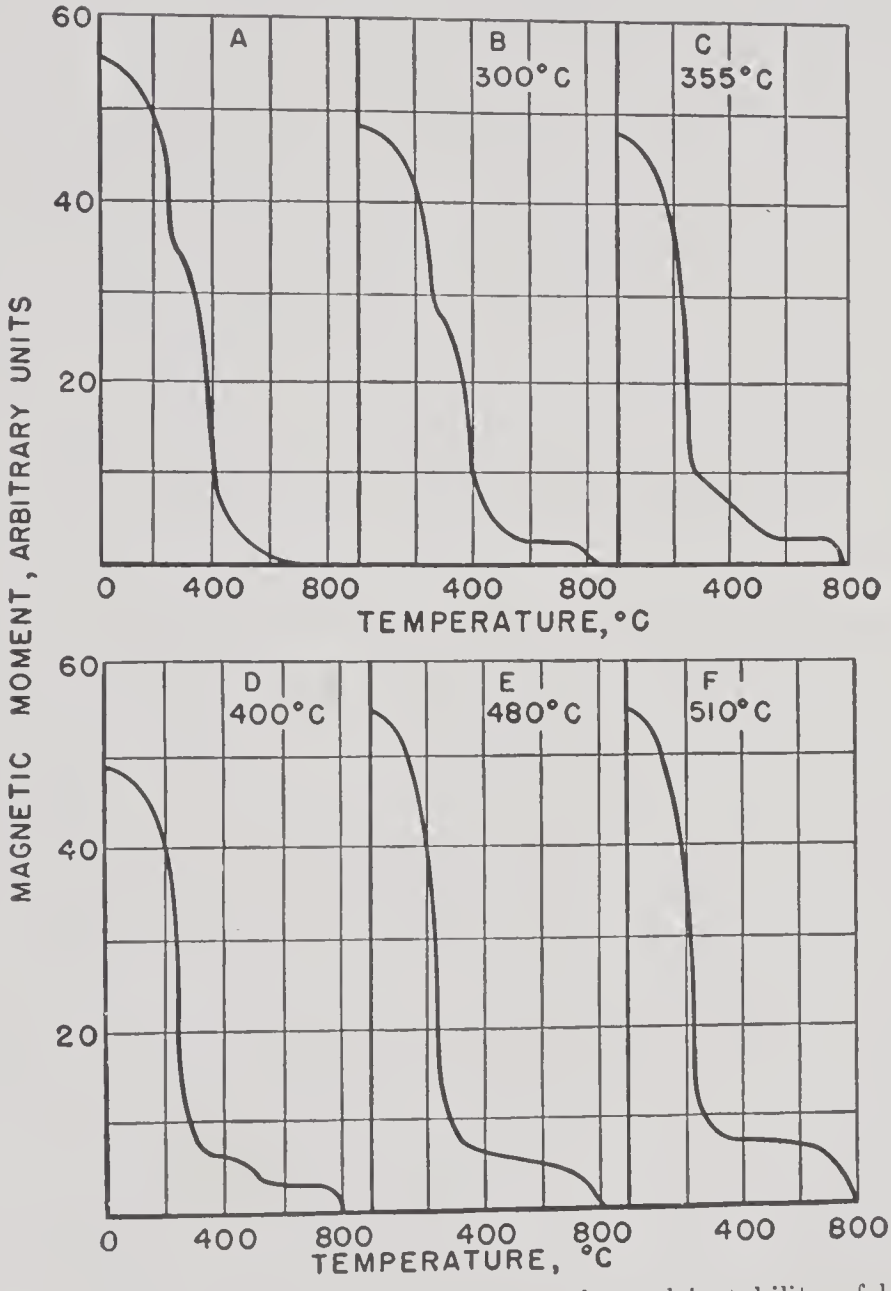


FIGURE 6–10. Thermomagnetic curves showing thermal instability of higher iron carbides, obtained by carburization at 205°C. Samples B-F kept at indicated reaction temperature for 0.5 hr, before thermomagnetic analysis as shown (100 Fe:1Cu:-0.25K_2CO_3 catalyst). Reproduced from reference 20.

corresponded to a mixture of cementite and Hägg Fe_2C; the magnetic balance probably was not sensitive enough to show the point of inflection between the Curie Points of these phases. Similarly the Curie Point in Figure 10*D* appears to be lower than that usually observed for Hägg Fe_2C. The heat treatment at 510°C caused the CP = 265°C carbide to disappear. This catalyst contained cementite and free iron.

These data are in general agreement with those of Herbst and Halle [19] on the transformation of hexagonal to Hägg Fe_2C.

Three catalysts were prepared by precipitation of iron oxide from solutions of iron nitrates (iron filings dissolved in dilute nitric acid) with sodium carbonate solution, at about the boiling temperature. For the first catalyst the precipitate was washed and dried. For the second

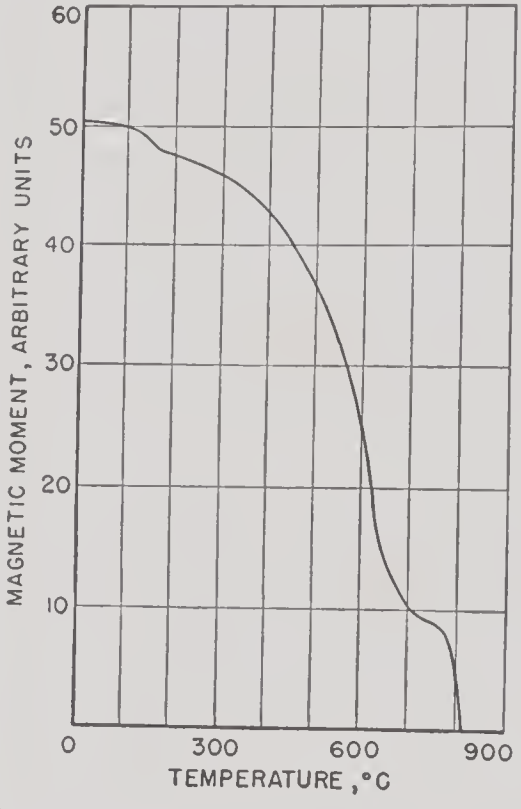


FIGURE 6–11. Thermomagnetic curve of unpromoted iron oxide, after carburization for 12 hr at 325°C and 0.1 atm; 8 l CO per hr per 10 g Fe. Reproduced from reference 20.

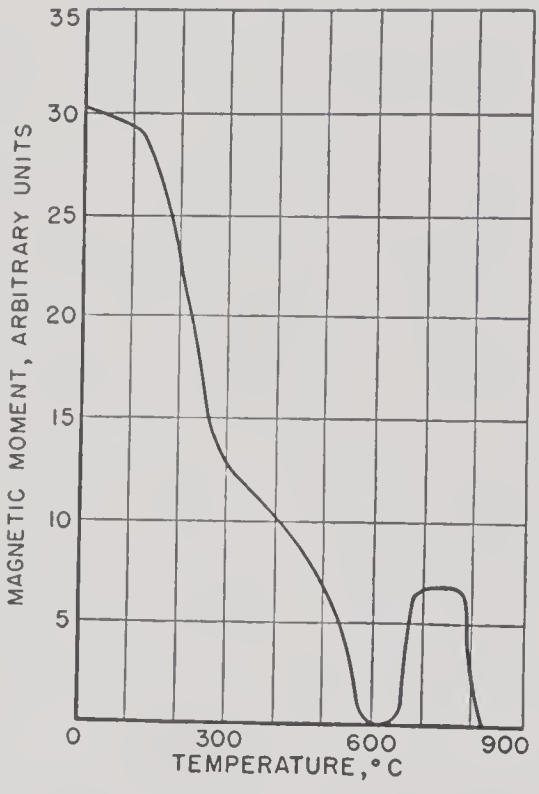


FIGURE 6–12. Thermomagnetic curve of alkalized (0.25% K_2CO_3) iron oxide, after carburization for 12 hr at 325°C and 0.1 atm; 8 l CO per hr per 10 g Fe. Reproduced from reference 20.

catalyst 0.25 part of potassium carbonate per 100 of iron was added to the washed precipitate before drying. In preparing the third catalyst, copper nitrate was added to the iron nitrate solution, and after precipitation and washing, the catalyst was alkalized with potassium carbonate, the resulting composition being $Fe:Cu:K_2CO_3 = 100:1.0:1.5$. These catalysts were carburized at 325°C and 0.1 atm with 8 l of carbon monoxide per 10 g of iron per hr.

The iron oxide catalyst carburized under these conditions for 12 hr showed only the Curie Points of magnetite and free iron (Figure 11). Carburization for 24 hr formed small amounts of Hägg Fe_2C and larger amounts of free iron; the remainder was magnetite.

After 12 hr of carburization of the iron oxide-potassium carbonate catalyst, the magnetic analysis (Figure 12) showed the presence of about 50 per cent Hägg Fe_2C and 50 per cent magnetite. The abrupt rise in the curve at 600°–700°C was due to reduction of magnetite to free iron by carbide or free carbon. A 25-hr carburization resulted in a larger

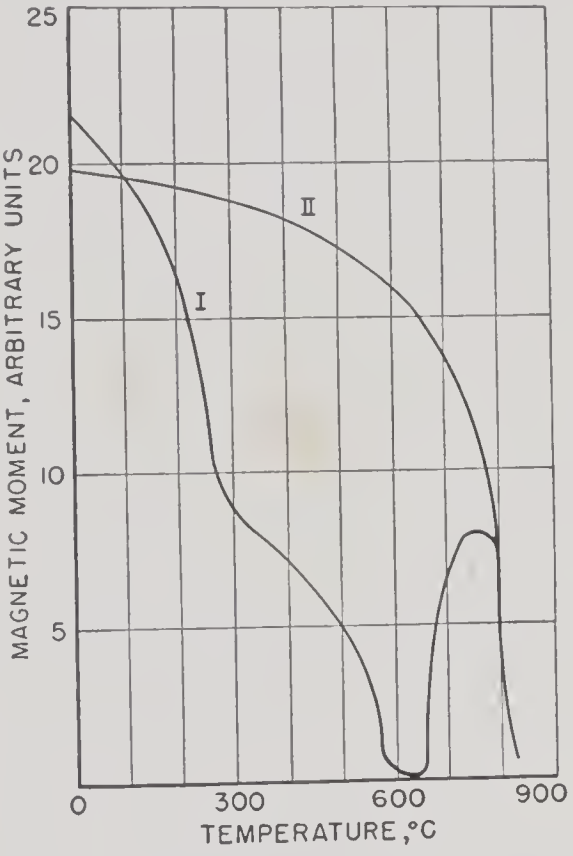


FIGURE 6–13. Thermomagnetic curves of alkalized (0.25% K_2CO_3) iron oxide, after carburization for 25 hr at 325°C and 0.1 atm; 8 l CO per hr per 10 g Fe. I, freshly carburized sample; II, after heating to 800°C. Reproduced from reference 20.

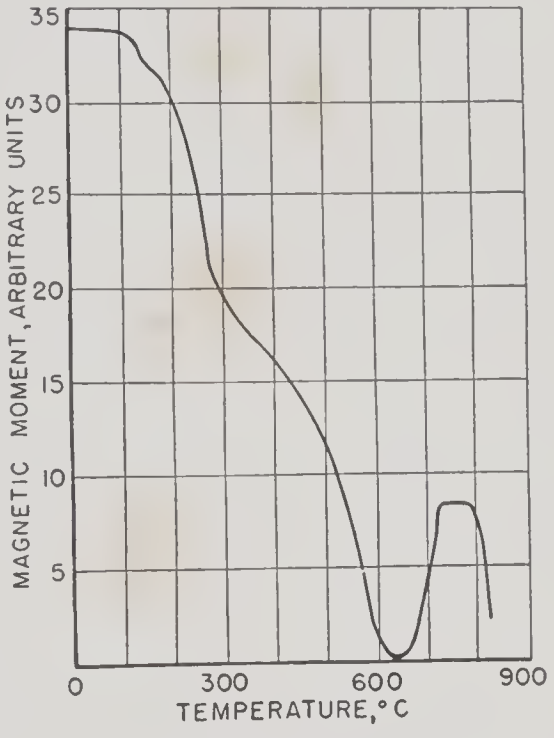


FIGURE 6–14. Thermomagnetic curve of Fe:Cu:K_2CO_3 (100:1:1.5) catalyst, after carburization for 0.5 hr at 325°C and 0.1 atm; 8 l CO per hr per 10 g Fe. Reproduced from reference 20.

fraction of Hägg carbide and less magnetite, as shown in Figure 13, curve I, and again free iron was formed above 600°C. Heating at 800°C (curve II) converted this sample to free iron.

The iron oxide-copper oxide-potassium carbonate catalyst was carburized at a considerably greater rate under the same conditions. In 30 min this catalyst (Figure 14) was carburized to an extent about equal to that of the iron oxide-potassium carbonate catalyst after 12 hr. The catalyst containing copper and alkali was completely converted to Hägg Fe_2C in 12 hr, as shown in Figure 15. Carburization for 25 and 62 hr (Figure 16) also formed Hägg carbide, and heat treatment at 800°C

completely converted the Fe_2C to cementite. Since no free iron was formed, it appears that no magnetite was present in the sample.

Hofer, Peebles, and Cohn [21] carburized samples of a reduced iron synthetic-ammonia catalyst (Fe-MgO-K_2O) and an iron oxide-copper oxide-potassium carbonate catalyst in carbon monoxide at atmospheric pressure and 238° and 188°C, respectively, until carbon equivalent to

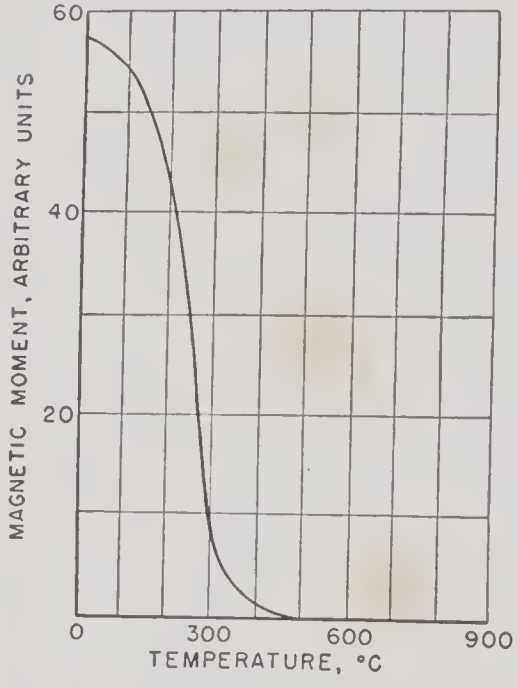


FIGURE 6–15. Thermomagnetic curve of Fe:Cu:K_2CO_3 (100:1:1.5) catalyst, after carburization for 12 hr at 325°C and 0.1 atm; 8 l CO per hr per 10 g Fe. Reproduced from reference 20.

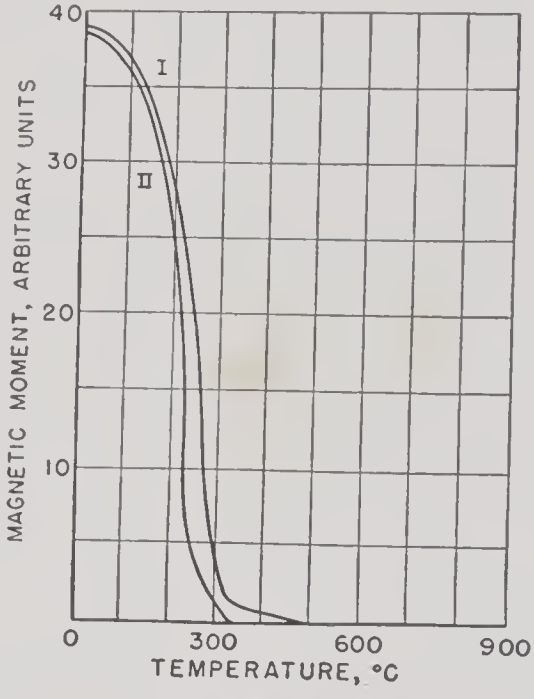


FIGURE 6–16. Thermomagnetic curves of Fe:Cu:K_2CO_3 (100:1:1.5) catalyst, after carburization for 25 hr (also 62 hr) at 325°C and 0.1 atm; 8 l CO per hr per 10 g Fe. I, freshly carburized sample; II, after heating to 800°C. Reproduced from reference 20.

Fe_2C was deposited, as shown in Figure 17. X-ray diffraction patterns indicated a progressive formation of the Hägg and hexagonal carbides in the synthetic-ammonia and precipitated catalysts, respectively. The hexagonal carbide was shown to decompose to the Hägg carbide at about 300°C, and it in turn decomposed to cementite at about 550°C.

Podgurski, Kummer, DeWitt, and Emmett [22] studied formation and stability of carbides in fused iron synthetic-ammonia catalysts, as well as the adsorption of carbon monoxide and hydrogen on carbided catalysts. The catalysts used were as follows: 910—pure Fe_3O_4, and 423—72.26 per cent Fe, 2.26 Al_2O_3, 0.67 SiO_2, and 0.21 ZrO_2.

[22] H. H. Podgurski, J. T. Kummer, T. W. DeWitt, and P. H. Emmett, *ibid.*, to be published.

Two methods of carburization of reduced catalysts were used: (*a*) with carbon monoxide, and (*b*) with saturated hydrocarbons, such as propane, butane, and pentane. The carburization with carbon monoxide is a highly exothermic reaction, and if the rate of carburization is very high, the temperature of the catalyst may greatly exceed the furnace temperature. The authors attributed to local overheating the formation of free carbon which is frequently produced in the carburization of

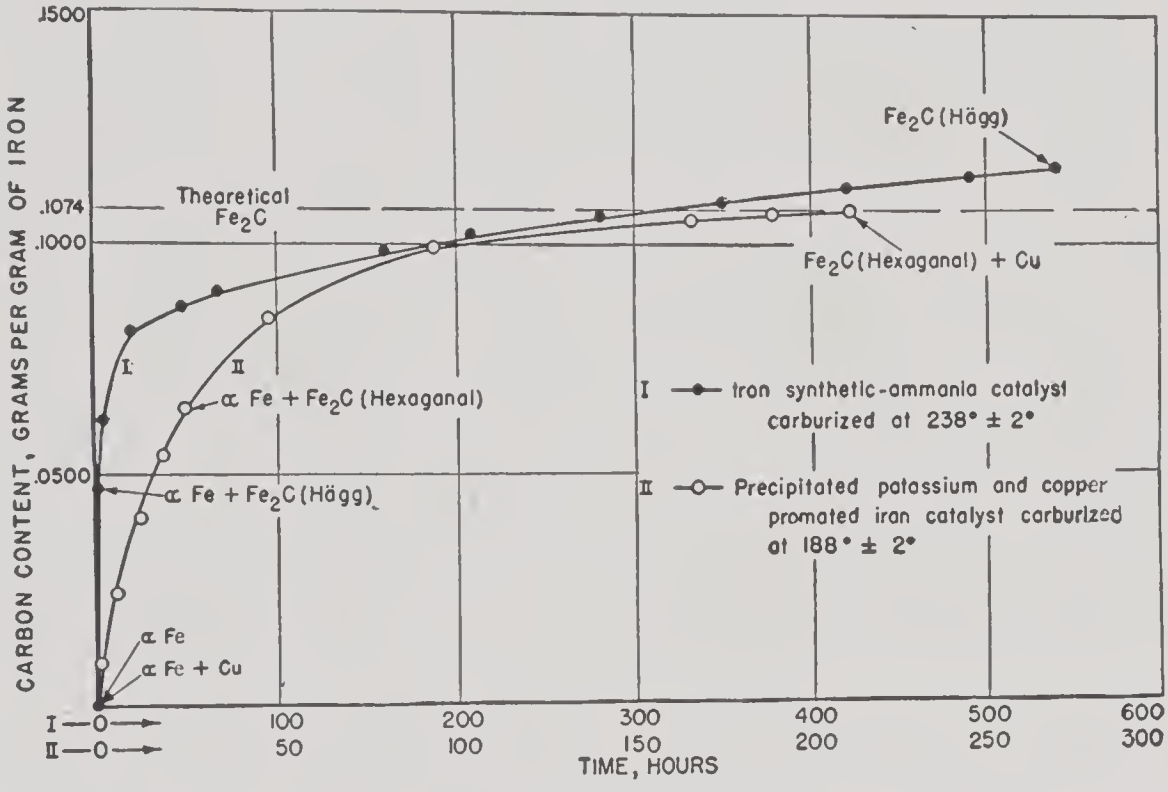


FIGURE 6–17. Carburization of two types of iron Fischer-Tropsch catalysts. Reproduced by permission from reference 21.

this type of catalyst. If the initial rate of carburization is kept low by starting the experiment at a low temperature, it is possible to prepare carbides without producing free carbon. Thus, for catalyst 423, carburization in carbon monoxide for 22 hr at 225°C plus 35 hr at 275°C yielded a carbide of 7.1 per cent carbon as compared with 9.67 per cent for Fe_2C. Samples carburized in carbon monoxide were shown to contain small amounts of oxygen, *ie*, roughly 1 atom of oxygen per molecule of nitrogen in the physically adsorbed monolayer, V_m (see p 52 of Chapter 2).

Carburization of iron Fischer-Tropsch catalysts with saturated hydrocarbons is a unique method of preparing carbides which would be simple and economical. Carburization with hydrocarbons is not a highly exothermic reaction and presents no serious problem of temperature control of the catalyst bed. In the carburization of catalyst 423 in *n*-butane

at 300°C, the sample contained 4.3, 6.9, and 7.5 per cent of carbon after 1.3, 9, and 18 hr, respectively. Butane treatment for longer periods or at higher temperatures did not appreciably increase the percentage of carbon above 7.5 per cent, nor did carbon monoxide treatment after carburization in butane to 7.5 per cent carbon cause any appreciable change in carbide content. The authors suggested that this incomplete carburization might result from complete covering of the outer layers by the carbide from butane and disappearance of free iron from the surface. Carburization with carbon monoxide at 200°C to 1 per cent of carbon greatly inhibited the rate of subsequent carbiding in butane.

Carbides prepared at 275°C by carbon monoxide or hydrocarbon treatment gave the x-ray diffraction pattern of the Hägg carbide. Both these carbides were partially converted to cementite in 3 hr *in vacuo* at 500°C. However, at 500°C the cementite prepared from the Hägg carbide produced by carbon monoxide treatment decomposed to iron and carbon at a much slower rate than the cementite from Hägg carbide produced by butane treatment. The oxide on the carbides prepared from carbon monoxide was probably responsible for the increased stability of the cementite.

The Hägg carbide in fused catalysts was observed to decompose very slowly to cementite at 400°C, and at 500°C this rate was fairly rapid. At 600°C, the Hägg carbide was rapidly converted to iron and carbon. Samples carburized only to a value equivalent to the carbon content of Fe_3C decomposed more rapidly than those of composition approximately Fe_2C. Apparently, the reaction

$$Fe_2C + Fe \rightarrow Fe_3C \qquad (1)$$

is more rapid than the decomposition to cementite and free carbon. Catalyst 423, when carburized in carbon monoxide to 2.5 per cent carbon, at 210°C, gave the x-ray diffraction pattern of hexagonal carbide. After further carburization to 6.5 per cent carbon, the x-ray diffraction patterns showed lines of both hexagonal and Hägg carbide. It was suggested that the hexagonal carbide may be an intermediate in the formation of Hägg carbide. Copper in a fused synthetic-ammonia catalyst was found to stabilize the hexagonal carbide.

The chemisorption of carbon monoxide was used to estimate the amount of free iron in the catalyst surface of reduced and carbided iron catalysts (see pp 64, 68, and 476). Chemisorption of carbon monoxide at −195°C on catalysts 910 and 423 as a function of the per cent carbidic carbon is shown in Figure 18. With reduced pure Fe_3O_4 the ratio of chemisorbed carbon monoxide:nitrogen monolayer decreased sharply with carbon content and approached a very low value at about 4 per

cent of carbon. With promoted catalyst 423 the initial ratio was lower than with 910, because of the accumulation of promoters on the surface, but the ratio decreased less rapidly with increasing carbide content. For catalysts carbided with carbon monoxide, the chemisorbed carbon monoxide decreased to essentially zero at 9.5 per cent of carbon, as compared with 7.8 per cent of carbon for the carbide from butane. Thus, the presence of carbide decreased the chemisorption of carbon monoxide;

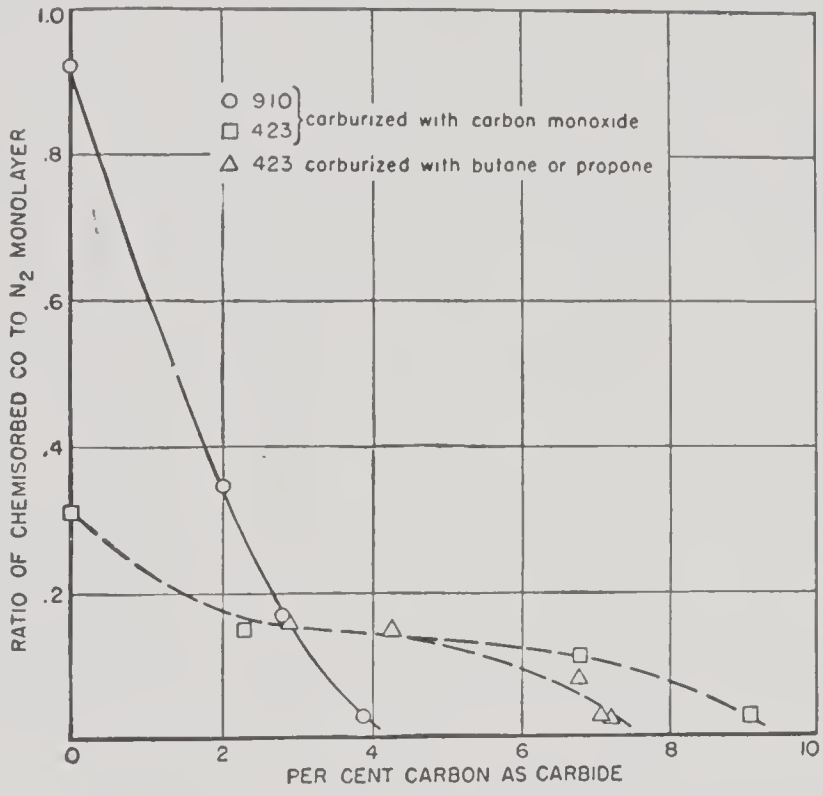


FIGURE 6–18. The decrease in carbon monoxide chemisorption at −195°C with the amount of Hägg carbide. From data of reference 22.

however, with promoted catalysts the chemisorption did not approach zero until the sample was fairly completely carbided. This suggests that the carbide does not accumulate at the surface but diffuses through the iron lattice and probably deposits on nuclei of Fe_2C. Evidence was presented for a loosely held chemisorption that occurs on partially carbided samples at −78° and −46°C.

On completely carbided samples (9.1 per cent carbon from carbon monoxide or 7.5 per cent carbon from butane) no detectable chemisorption of carbon monoxide occurred at 100° and 200°C. A similar, reduced catalyst chemisorbed considerable quantities of carbon monoxide at 50° and 100°C and began to form carbide at 150°C.

Adsorption isobars of hydrogen on reduced iron are characterized by two maxima corresponding to type *A* (−78°C) and type *B* (100°C) chemisorptions (p 58, Chapter 2). Type *A* chemisorption was virtually

eliminated on partially carbided samples, but type *B* was almost as large as on reduced catalysts, except for samples that were nearly completely carburized and for which the type *B* chemisorption was appreciably decreased. Type *B* chemisorption at 100°C was lower for butane carbides than for those from carbon monoxide. This may be due either to enhanced hydrogen chemisorption of the oxide formed in carbon monoxide treatment or to residual hydrogen from the butane carbiding.

Recently, Jack [18] published extensive x-ray diffraction studies of the carbides, nitrides, and carbonitrides of iron. The Hägg carbide, termed "iron percarbide" by Jack, was shown to have either an orthorhombic or a hexagonal unit cell, and its density as computed from lattice parameters was 7.2 g per cc. The formula for this carbide was given as $Fe_{20}C_9$ ($Fe_{2.22}C$), which is very close to $Fe_{2.28}C$ observed by Pichler and Merkel.[20] The iron percarbide was prepared by treating iron nitride, Fe_2N, with carbon monoxide at 450°–500°C. Cementite was formed by this method at higher temperatures (600°C). This is an interesting method of preparing the carbides, since at temperatures as high as 600°C no free carbon was formed.

The nitrides of iron were prepared by passing ammonia at high space velocity over iron at 450°C. On carbon monoxide treatment the nitrogen was progressively eliminated, and a series of carbonitrides of variable composition was formed. If the treatment was continued sufficiently long, all the nitrogen was eliminated. These carbonitrides could also be formed by treating the "percarbide" with ammonia. In the carbonitrides the atom concentration of C + N remained almost constant (33.5–36.0 atom per cent), and the crystal structure of Fe_2N persisted in the range Fe_8N_4 to Fe_8C_3N. When nitrides of lower nitrogen content than Fe_2N were carburized with carbon monoxide, the carbon content increased rapidly without replacing nitrogen until the total nitrogen plus carbon atom concentration was about 34 per cent. The rate of carbiding of the nitrides was considerably greater than that of α-iron, and no free carbon was deposited. Jack suggested that the body-centered α-iron is resistant to carbide formation. In formation of the nitride, the lattice expands first to face-centered cubic and then to the hexagonal close-packed structure, and these structures are more easily penetrated by carbon.

The studies of Jack provide an interesting method of preparing the iron percarbide (Hägg) without excessive carbon deposition and also a method of pretreating iron catalysts to form bulk phases with unique crystal structure and composition. Nitrides and carbonitrides of iron have unusual properties as Fischer-Tropsch catalysts (see p 549).

CARBIDES OF RUTHENIUM

Pichler [23] states that "no ruthenium carbide is known to form under conditions of the synthesis. The formation of ruthenium carbide is possible at very high temperatures."

FORMATION OF ELEMENTAL CARBON

Some data on the formation of elemental or free carbon have already been presented in connection with the formation of carbides of nickel, cobalt, and iron. With nickel and cobalt, carburization in carbon monoxide may be characterized by two temperatures. Below the lower temperature only carbide is formed, above the higher temperature only elemental carbon, and between these temperature limits both carbidic carbon and elemental carbon are formed. For nickel, these temperatures are about 285° and 420°C, and for cobalt, 210° and 275°C. With iron the data are not as clear cut, but it appears that fairly pure carbides can be formed below 225°–275°C. Mixtures of carbides and free carbon can be formed at temperatures at least as high as 400°C.

There is considerable literature on the formation of free carbon from carbon monoxide. Fischer and Dilthey [24] and Waugenheim [25] studied the formation of free carbon on iron at 350°–500°C. As the reaction proceeded, the iron disintegrated and was carried into the free-carbon phase, the reaction continuing until the percentage of iron was about 1 per cent. This iron was chiefly in the form of cementite. It was not possible to prepare iron-free carbon by this method. Fischer and Bahr [26] showed that, when an iron-copper catalyst was carburized with carbon monoxide at 500°C, the carbon contained copper as well as iron. This suggests that the iron and copper were dispersed by mechanical means.

Apparently, at least part of the free carbon is formed within the metal lattice, and the carbon deposit increases in size until the metal lattice splits. This implies that dissolved or carbidic carbon formed at the metal surface diffuses in the metal lattice and deposits as free carbon on a particle of carbon or other nuclei. The hypothesis that carbides are intermediates in free-carbon formation is attractive, but it is by no means

[23] H. Pichler, Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen, *U. S. Bur. Mines Spec. Rept.* (1947), 158 pp. Translation reproduced in T.O.M. Reel 259, Frames 467–654.

[24] F. Fischer and P. Dilthey, *Brennstoff-Chem.*, 8, 388 (1927); 9, 24 (1928); *Ges. Abhandl. Kenntnis Kohle*, 8, 234 (1929).

[25] F. Waugenheim, *ibid.*, 8, 227 (1929).

[26] F. Fischer and H. Bahr, *ibid.*, 8, 255 (1929).

proved.[2] Studies of Kummer, DeWitt, and Emmett [27] on carbiding of iron catalysts with $C^{14}O$ suggest that diffusion of carbon in the iron lattice is rapid at temperatures as low as 200°C.

It is also possible to form carbidic and elemental carbon by the decomposition of hydrocarbons. As shown in Chapter 2, all hydrocarbons except methane and ethane are thermodynamically unstable with respect to carbon as graphite and hydrogen at temperatures above 100°C. With higher paraffinic and all olefinic hydrocarbons it is thermodynamically possible to form Hägg Fe_2C and cementite at temperatures above 200°C. Schmidt and Osswald [28] observed that free and carbidic carbon was formed by decomposition of acetylene on nickel. Methods of suppressing carbon formation are not well developed. Baukloh and Hellbrügge [29] state that the presence of chromic oxide in iron decreases the rate of formation of free carbon from carbon monoxide.

Carbon deposition during the synthesis usually does not occur in appreciable amounts on cobalt or nickel catalysts unless the catalyst is operated at excessively high temperatures. With iron catalysts, carbon deposition usually accompanies the synthesis. Swelling and disintegration of particles accompanying carbon deposition are a serious problem in the synthesis with iron catalysts. Very little has been published regarding carbon deposition in the synthesis, and it has not been established whether the carbon results from the decomposition of carbon monoxide or hydrocarbons.

Pichler and Merkel [20] determined free carbon in iron catalysts used in the synthesis by their acid decomposition method, as shown in Table 9. A number of catalysts pretreated by carburization in carbon monoxide were analyzed for free carbon after use in the synthesis. Sizable amounts of free carbon were formed in the pretreatment. In all the experiments in Table 9, the free-carbon content increased with time. In experiment 3 the large amount of carbon was due in part to the high final temperature of operation. The rate of carbon deposition usually paralleled the activity in the synthesis. Thus in experiment 4, the catalyst which gave only a 40 per cent contraction contained much less carbon after 11 weeks than the more active catalyst in experiment 1 after 3 weeks. The alkali content of iron catalysts is the most important composition variable, since the rate of free and carbidic carbon formation increases with increasing alkali content. Carbon formation increased with

[27] J. T. Kummer, T. W. DeWitt, and P. H. Emmett, *J. Am. Chem. Soc.*, **70**, 3,632 (1948).

[28] J. Schmidt and E. Osswald, *Z. anorg. u. allgem. Chem.*, **216**, 85 (1933).

[29] W. Baukloh and J. Hellbrügge, *Arch. Eisenhüttenw.*, **15**, 163 (1941); *Brennstoff-Chem.*, **23**, 87 (1942).

TABLE 9. FORMATION OF FREE CARBON DURING SYNTHESIS [a]

(Catalysts pretreated with carbon monoxide at 0.1 atm and 325°C and used in synthesis with $2H_2 + 3CO$ at 15 atm.)

Experiment	Weeks of Operation	Temperature, °C	Contraction, per cent	Free Carbon, g per 10 g iron
1	0	...	..	1.75
	1	235	52	2.12
	3	235	55	2.37
2	0	...	..	1.85
	16	235	50	3.92
3	0	...	..	2.21
	78	235–285	55–45	7.97
4	0	...	..	1.75
	11	235	40	2.02

[a] H. Pichler and H. Merkel; see reference 20.

the ratio of carbon monoxide:hydrogen in the synthesis gas, as shown in Table 10. With $4H_2$:1CO gas the free carbon decreased during the synthesis, and it increased only slightly with $2H_2$:1CO gas. With $2H_2$:3CO gas, the free carbon increased at a greater rate. Thus, formation of excessive amounts of free carbon may be avoided by using hydrogen-rich gas and low temperatures.

TABLE 10. FORMATION OF FREE CARBON AS A FUNCTION OF SYNTHESIS GAS COMPOSITION [a]

(Catalysts presumably inducted as described in previous table. Pressure of operation = 15 atm.)

Experiment	Temperature, °C	Days of Operation	Ratio of H_2:CO in Synthesis Gas	Contraction, per cent	Free Carbon, g per 10 g Fe
1	190	0	4:1	..	2.21
	200 [b]	60	"	30	1.88
2	210	0	2:1	..	2.21
	225 [b]	151	"	35	2.51
3	235	0	2:3	..	1.85
	240 [b]	112	"	50	3.92

[a] H. Pichler and H. Merkel; see reference 20.

[b] Temperature required to maintain constant conversion.

KINETICS OF FORMATION OF CARBIDIC AND FREE CARBON

The kinetics of the formation of cobalt carbide, Co_2C, from carbon monoxide on cobalt-thoria-kieselguhr catalysts has been studied by Craxford and Rideal,[30] Eidus and Zelinskii,[31] and Weller.[32] The experiments of Craxford and Rideal were made in a static system, and thus

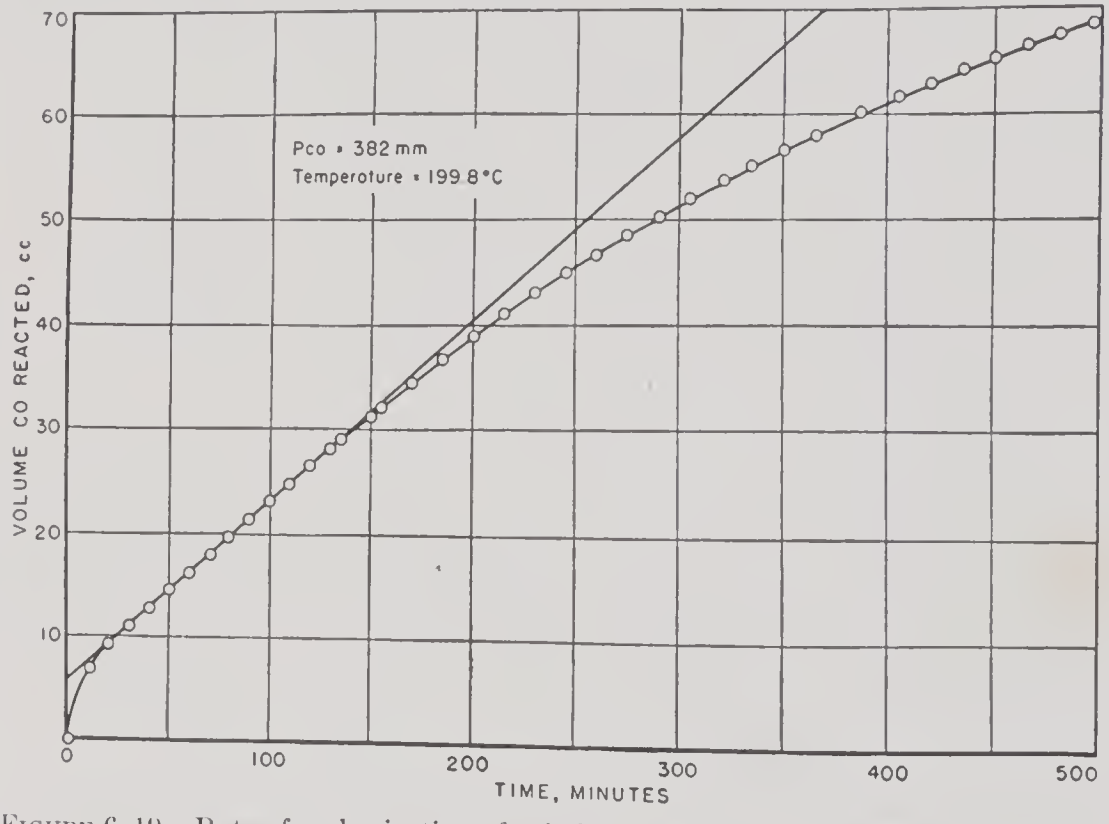


FIGURE 6–19. Rate of carburization of cobalt-thoria-kieselguhr catalyst 108B. Reproduced by permission from reference 32.

the results may be somewhat uncertain. Eidus and Zelinskii and Weller used flowing systems which provide more certain kinetic data. Craxford and Rideal observed a rapid rate of carburization in the first few minutes which was followed by a lower, constant rate for at least 20 hr. Eidus and Zelinskii did not determine the initial rate but observed a constant rate from their first reading (at 5 hr) to 15–20 hr, the rate decreasing after this time. Weller observed a rapid initial rate followed by a constant rate for 30–150 min, the rate decreasing after 150 min, as shown in Figure 19. The rate of this constant intermediate portion was

[30] S. R. Craxford and E. K. Rideal, *J. Chem. Soc.*, 1,604 (1939).

[31] Y. T. Eidus and N. D. Zelinskii, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 190 (1942).

[32] S. Weller, *J. Am. Chem. Soc.*, **69**, 2,432 (1947).

not greatly dependent upon pressure of carbon monoxide from 0.07 to 0.6 atm, as expressed by the equation,

$$\text{rate} = k p_{CO}^{0.20\text{-}0.26}$$

Weller [32] summarized and compared the rates and overall activation energies of carburization and synthesis, as shown in Table 11. The data

Table 11. Rates and Activation Energies of Carbiding and Synthesis on $Co:ThO_2:Kg = 100:18:100$ Catalysts

		Craxford and Rideal [a]	Eidus and Zelinskii [b]	Weller [c]
Rates (g C per g Co per hr $\times 10^4$) at 200°C				
Carbiding with CO	1st stage	35 [d]	..	1,000–2,000 [d]
	2nd stage	0.8 [e]	42 [f]	60–65 [h]
Synthesis		280	~430	560
Apparent activation energies, kcal per mole				
Carbiding with CO	1st stage	10.0 [g]	....	....
	2nd stage	18.0 [g]	14.8 [f]	31.0 [h]
Synthesis		9.5		26.5

[a] S. R. Craxford and E. K. Rideal; see reference 30.
[b] Y. T. Eidus and N. D. Zelinskii; see reference 31.
[c] S. Weller; see reference 32.
[d] First minute.
[e] After 2–3 hr.
[f] First 5 hr.
[g] First few minutes.
[h] Twenty–150 min.

are somewhat inconsistent; at least some of the differences are due to the different experimental methods. All the data indicate that the rate of the second stage of carbiding was lower than the rate of synthesis. The data of Weller indicate that the initial rate of carbiding was greater than the rate of synthesis, and thus this carbide may be an intermediate in the synthesis. The activation energies of Weller may be regarded as the most certain, because his experimental method was better than that of either Craxford and Rideal or Eidus and Zelinskii, and because Weller's activation energy for synthesis, as determined by his experimental method, agreed satisfactorily with those found in experiments in small catalyst-testing reactors.[33]

[33] R. B. Anderson, A. Krieg, B. Seligman, and W. O'Neill, *Ind. Eng. Chem.*, **39**, 1,545 (1947).

The hydrogenation of cobalt carbide to methane was very much more rapid than the formation of carbide from carbon monoxide, as shown by the data of Hofer and Weller in Figures 2, 3, 4, and 20. The work of

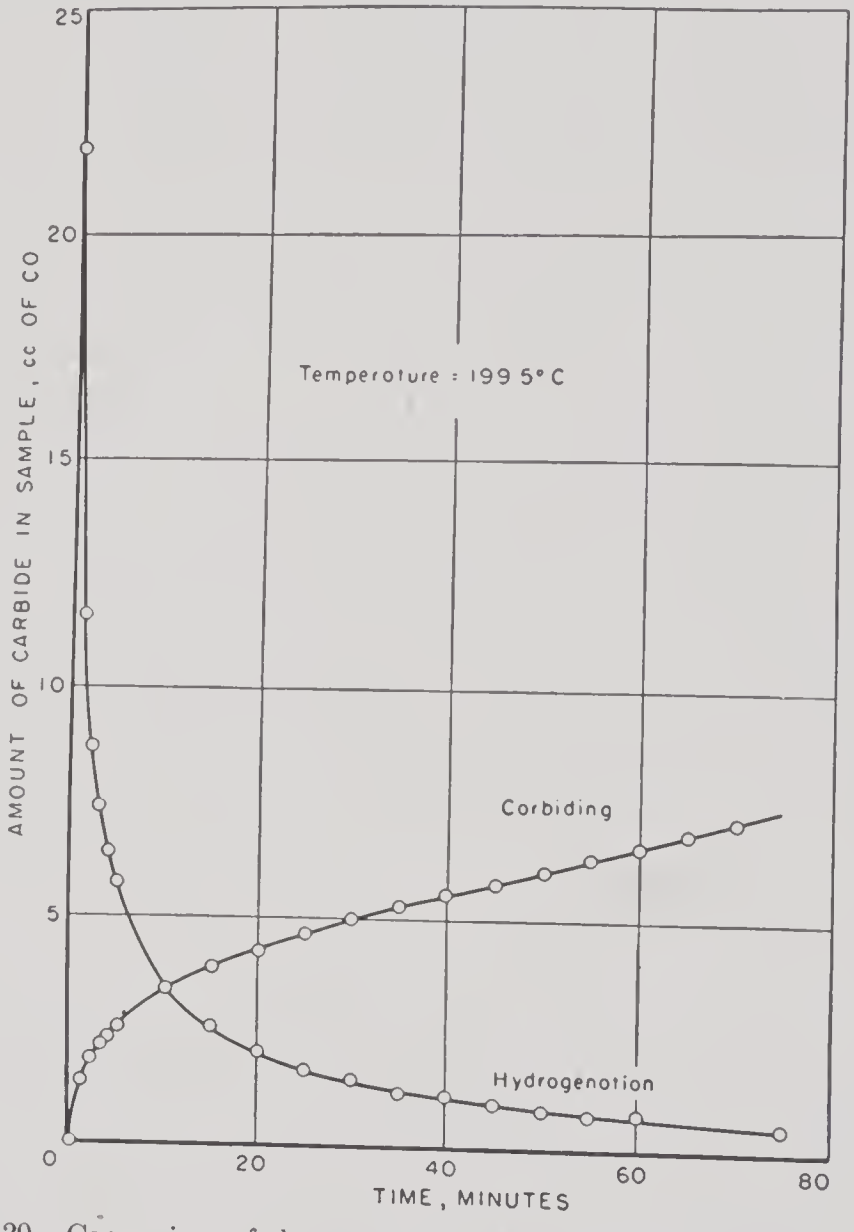


FIGURE 6–20. Comparison of the rates of formation and hydrogenation of carbide in cobalt-thoria-kieselguhr catalyst 108B. Reproduced by permission from reference 32.

Hofer [12] on the thermal decomposition of cobalt carbide has been discussed on p 474. The high apparent activation energy of decomposition, 54.3 kcal per mole, indicates that at higher temperatures the rate of decomposition may exceed the rate of carbide formation.

Only a few kinetic studies of the formation and hydrogenation of carbides of iron are available, and most of them have been discussed pre-

viously. Podgursky, Kummer, DeWitt, and Emmett [22] observed activation energies for the formation of Hägg carbide with carbon monoxide that varied from 30 to 35 kcal per mole. The hydrogenation of carbides of iron is usually considerably slower than their formation.

Eidus [34] compared the rates of carburization and synthesis of nickel-manganese-alumina, cobalt-thoria, and iron-copper-thoria-potassium carbonate catalysts, all of which were supported on marshallite, as shown in Table 12; these rates were compared at 30 min and at 10 hr. After

Table 12. Comparison of Rates of Synthesis and Carbiding [a]

Catalyst	Rates Based on Gas Contraction				Ratio of Rate of Synthesis: Rate of Carbiding	
	At 30 min		At 10 hr			
	Synthesis	Carbiding	Synthesis	Carbiding	At 30 min	At 10 hr
Cobalt (190°–210°C)	2.4–4.0	0.2–0.8	3.2–3.6	0.07–0.18	5.2–10.7	19–46.5
Nickel (200°–210°C)	3.0–4.5	0.6–0.8	3.6–3.8	0.13–0.21	5.1–5.7	17–29
Iron (230°–260°C)	1.26–1.36	0.6–0.8	1.3–1.8	1.16–0.23	1.6–2.1	8

[a] Y. T. Eidus; see reference 34.

10 hr, the rate of carbiding had decreased to about one-fourth of the initial rate, but the rate of synthesis remained essentially constant. For cobalt and nickel catalysts the ratio of the initial rates of synthesis:carbiding was more than 5. For the iron catalyst the ratio of initial rates of synthesis:carbiding was 1.6–2.1. From these data, Eidus concluded that the synthesis on iron catalyst could occur by a carbide intermediate mechanism, but that the carbide mechanism was unlikely for the synthesis on cobalt and nickel catalysts. However, Weller found that the rate of carbiding of a cobalt catalyst during the first minute was greater than the rate of synthesis. Comparison of the rates of synthesis and carbiding is not a satisfactory way of testing the carbide hypothesis. For example, even if the synthesis does proceed by a carbide mechanism,

[34] Y. T. Eidus, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, **41**, 190 (1942).

the rates of carbiding and synthesis may be dependent upon different rate-controlling steps. However, these experiments indicate that carbides may possibly be intermediates, but do not eliminate other reaction mechanisms.

KINETICS OF THE FISCHER-TROPSCH SYNTHESIS

Although the Fischer-Tropsch synthesis has been studied extensively, many aspects of its kinetics are not well understood. Many of the experiments reported in the literature were improperly designed for simple and unambiguous kinetic interpretation. Experiments conducted at "maximum conversion to liquid and solid hydrocarbons" or rather complete conversion, while of practical interest, are of little value for kinetic consideration.

In this section we have made considerable use of plots of per cent conversion against the reciprocal of space velocity for data obtained at constant temperatures, and in some cases yields expressed as grams of product per cubic meter are plotted against the reciprocal of space velocity. Curves of this type usually correlate data for variation of flow or volume of catalyst at constant temperature unless mass transfer is a rate-determining step. The slope of these curves is the differential reaction rate, expressed as volume of reactant consumed per volume of catalyst per hour, and these rates may be related to the partial pressures of components at the point where the slope of the conversion curve is determined.

KINETICS OF THE FISCHER-TROPSCH SYNTHESIS WITH NICKEL CATALYSTS

All experiments with nickel catalysts reported in this section were made at atmospheric pressure. Fujimura and Tsuneoka [35] studied the effect of H_2:CO ratio on the synthesis with a precipitated nickel catalyst (Ni-Mn-Al_2O_3-kieselguhr) at 190° and 200°C. In these experiments the extent of conversion was maintained so high that either hydrogen or carbon monoxide was almost completely consumed, and hence the rate of reaction should not be related to gas composition. The usage ratio of H_2:CO was about 2 for wide variations of gas composition, as shown in Table 13. As should be expected, the maximum yield per unit volume of synthesis gas was observed for $2H_2$ to 1CO gas.

[35] K. Fujimura and S. Tsuneoka, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **25**, 137 (1934).

TABLE 13. HYDROGEN TO CARBON MONOXIDE USAGE RATIO OF THE FISCHER-TROPSCH SYNTHESIS ON NICKEL CATALYSTS [a]

H_2:CO Ratio of Synthesis Gas	Temperature, °C	Usage Ratio, H_2:CO
0.315	200	1.16
0.315	210	1.12
0.932	200	1.73
2.01	200	2.12
2.63	190	2.31
2.63	200	2.20
4.74	180	2.38
4.74	190	2.68 [b]

[a] K. Fujimura and S. Tsuneoka; see reference 35.

[b] Very little liquid hydrocarbon formed under these conditions.

Tsuneoka and Fujimura [36] varied the weight of charge of a precipitated nickel catalyst (Ni-Mn-ThO_2-kieselguhr), while the flow of synthesis gas and temperature were kept constant. These data for $2H_2$:1CO and $1H_2$:1CO gas are presented in Figures 21 and 22, respectively. The rate

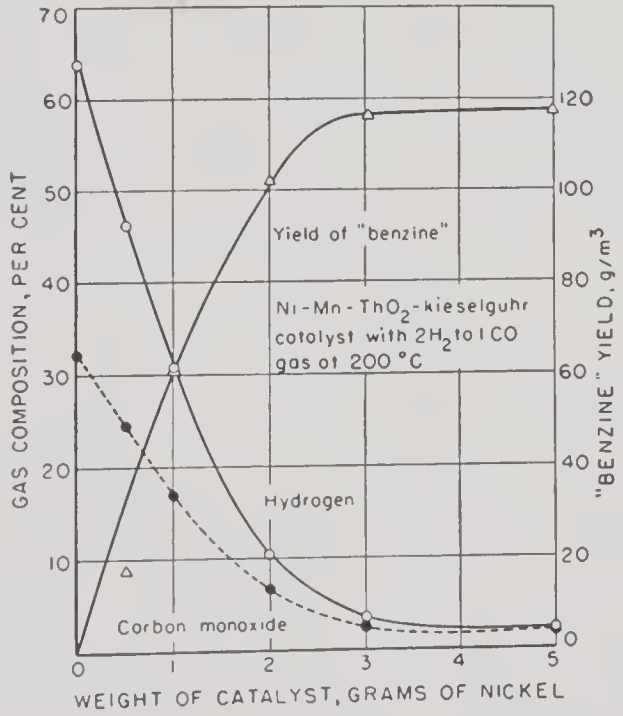


FIGURE 6–21. Variation of gas composition and yield of "benzine" with weight of catalyst charge at constant flow of synthesis gas. Reproduced from reference 36.

of synthesis was not very dependent upon partial pressures of reactants or products, since the rate curves were nearly linear even though the

[36] S. Tsuneoka and K. Fujimura, *J. Soc. Chem. Ind. Japan*, **37**, Suppl. binding, 463 (1934).

partial pressures varied over a wide range. The conversion-to-"benzine" curve flattened when about 80 per cent of one or the other of the reactants was consumed.

Aicher, Myddleton, and Walker[37] studied the synthesis on precipitated nickel catalyst (Ni-Mn-Al_2O_3-kieselguhr-hydrolyzed ethyl orthosilicate) in a flowing system, using $2H_2$:1CO and $1H_2$:1CO gas in the

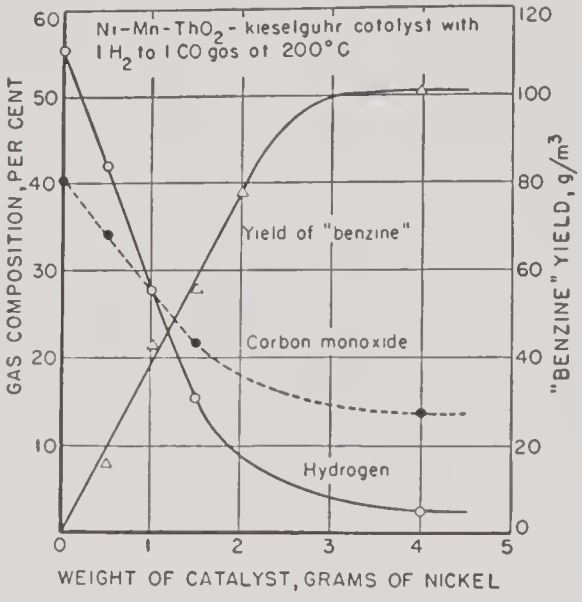


FIGURE 6–22. Variation of gas composition and "benzine" yield with weight of catalyst charge at constant flow of synthesis gas. Reproduced from reference 36.

temperature range 181°–206°C. In Figure 23 the formation of liquid hydrocarbons per cubic meter of $2H_2$:1CO gas is plotted against the reciprocal of space velocity at 198° and 205°C. The conversion to liquid hydrocarbons increased with decreasing space velocity (or increasing amount of catalyst at constant flow), the increase being slightly less than linear. Overall activation energies for the synthesis were computed from the variation of the flows of synthesis gas with temperature at a constant conversion. Values of 26.5, 27.3, and 29.1 kcal per mole were obtained at conversions to 60, 100, and 140 of liquid hydrocarbons per cu m, respectively. Similar data for $1H_2$:1CO gas (blue water gas) at 191°, 201°, 206°, and 207°C are presented in Figure 24. These data scattered more than those in the previous figure, and the rate curve was approximated by straight lines through the origin. From these lines apparent activation energies of about 23 kcal per mole were computed. Figures 23 and 24 are similar to Figures 21 and 22, and these also indicate that the rate was only slightly dependent upon partial pressures of components.

[37] A. Aicher, W. W. Myddleton, and J. Walker, *J. Soc. Chem. Ind. (London)*, **54**, 313T (1935).

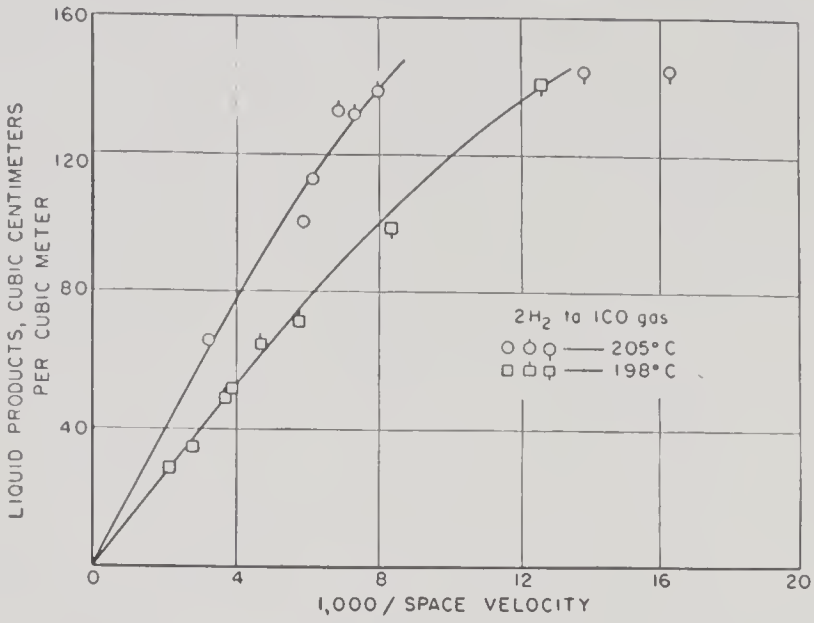


FIGURE 6–23. Yield of liquid hydrocarbon from a nickel catalyst as a function of the reciprocal of space velocity. Reproduced from data of reference 37.

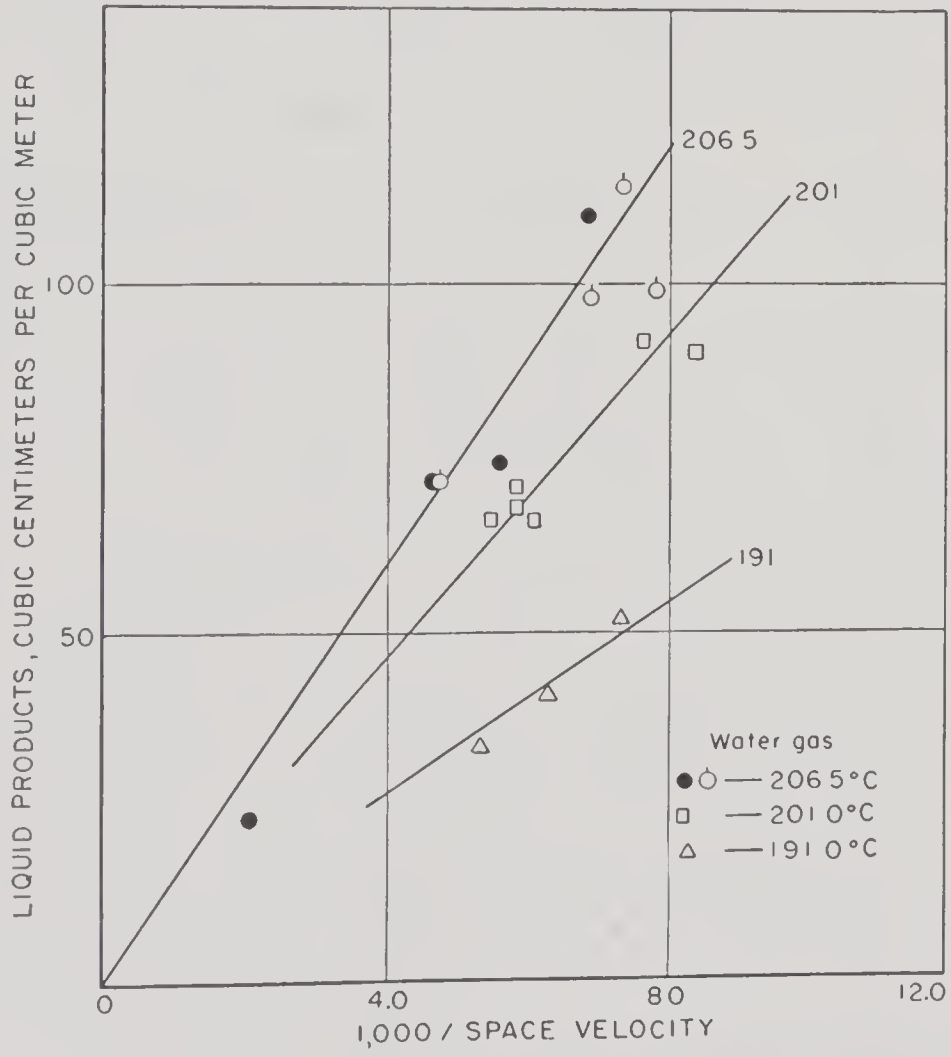


FIGURE 6–24. Yield of liquid hydrocarbons from a nickel catalyst as a function of the reciprocal of space velocity. Reproduced from data of reference 37.

Aicher, Myddleton, and Walker plotted the space-time-yield of liquid hydrocarbons against integrated averages of A/X, where A is the concentration of reactants and X the concentration of products, as shown in Figure 25. The increase in space-time-yield was approximately linear with the mean of A/X. These data appear inconsistent with the data of Figures 21–24. However, Figure 25 includes only the data for conversion to yields of liquid hydrocarbons greater than 111 cc per cu m, where the conversion curves had flattened considerably. In this range of conversion, it is possible that hydrocracking (described in the section on kinetics of cobalt catalysts, pp 514–519) was occurring to a major extent; this reaction, which increases with the concentration of products (X), would decrease the space-time-yield. The conclusion of these authors that the rate of reaction was decreased by adsorption of hydrocarbon products is probably not correct. Figure 25 suggests that operation in stages with the liquid hydrocarbon products removed after each stage would be advantageous, and at low flows of synthesis gas experiments in two stages gave higher yields of liquid hydrocarbons at the same flow per total volume of catalyst than in one-stage operation.

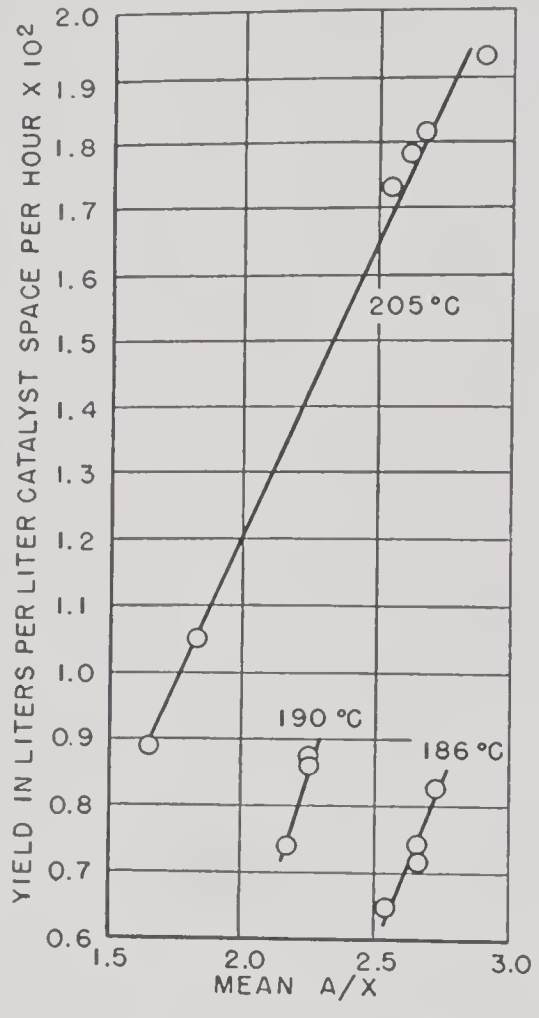
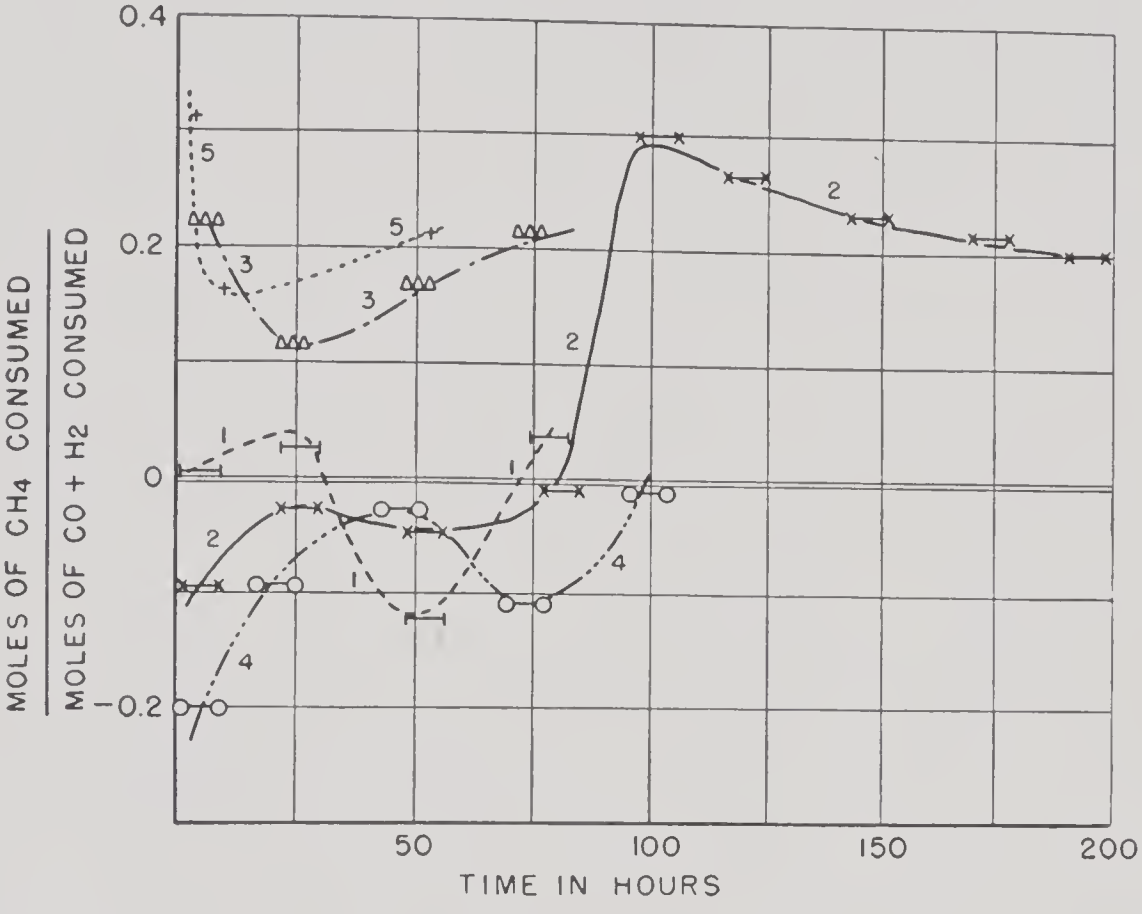


FIGURE 6–25. A plot of space-time-yield against the concentration of reactants A divided by the concentration of products X. Reproduced by permission from reference 37.

Myddleton and Walker [38] observed that the usage ratio of H_2:CO in the synthesis with nickel catalysts was about 2 for gases containing H_2:CO in the range of 0.67–2.5:1. Greater initial ratios than 2.5 favored the formation of methane and light hydrocarbons. Diluents such as nitrogen and excess hydrogen or carbon monoxide tended to increase the conversion of available gas. The data of Figures 22 and 24 indicate that large amounts of carbon monoxide do not retard the synthesis.

[38] W. W. Myddleton and J. Walker, *ibid.*, 55, 121T (1936).

Prettre and coworkers [39,39a] reported that large amounts of methane in the synthesis gas (25 per cent or more) not only decreased the amount of methane produced, but in many cases methane was consumed in the synthesis with Ni-Al_2O_3(or MnO)-kieselguhr catalysts. Figure 26 pre-



Curve 1, catalyst A 7 at 190 °C, 50 % CH_4

Curve 2, catalyst C.I. 1 at 190 °C, 50 % CH_4

Curve 3, catalyst C.I. 4 at 190 °C, 75 % CH_4

Curve 4, catalyst C.I. 4 at 190 °C, 25 % CH_4

Curve 5, catalyst C.I. 6 at 175 °C, 50 % CH_4

The length of the lines indicates the period in which the individual determinations were made.

FIGURE 6–26. Reproduced by permission from reference 39*a*.

sents the moles of methane consumed to moles of H_2 + CO consumed as a function of hours of testing for five experiments. With 75 per cent methane at 190°C and 50 per cent methane at 175°C the results for

[39] M. Prettre, *Rev. inst. Franç. pétrole et Ann. combustibles liquides*, **2**, 195 (1947); M. Prettre, C. Eichner, and M. Perrin, *Compt. rend.*, **224**, 278 (1947).

[39a] M. Perrin, "Recherches sur les syntheses d'hydrocarbures aliphatiques a l'aide des melange d'oxide de carbone et d'hydrogene," doctoral dissertation under Prof. M. Prettre, University of Lyon, 1948.

methane consumption were consistently high, approaching a ratio of $0.7CH_4$ to 1CO consumed.

With high concentrations of methane or at lower temperatures, the consumption of methane approached the maximum ratio of methane: carbon monoxide of 1 that was predicted by the thermodynamic data of Prettre (see Table 13, p 25, Chapter 1). Prettre postulated that this reaction occurs by the dissociative adsorption of methane with incorporation of these methyl or methylene groups into the hydrocarbon molecules being formed at the surface of the catalyst.

Craxford [40] has reported that methane is incorporated in the synthesis on cobalt catalysts. A cobalt catalyst was tested alternately with synthesis gas plus 50 per cent methane and with 50 per cent of nitrogen. The yield of oil was increased slightly and the yield of gasol more than four-fold by the presence of the methane. Craxford stated that these results would be expected if methane were dissociatively adsorbed and participated in a polymerization-depolymerization equilibrium at the catalyst surface. However, recent studies of Emmett and Kummer [41] indicate that methane is not incorporated on iron and cobalt catalysts. A mixture of synthesis gas and 50 per cent methane containing radioactive $C^{14}H_4$ was circulated over the catalyst, and the higher hydrocarbons produced were analyzed for C^{14}. These products, in no case, showed appreciable radioactivity. This tracer method is very much more reliable than comparison of net changes in gas composition, because analysis of these complex gas mixtures by Orsat-type analytical methods is possibly of somewhat uncertain accuracy. However, Perrin [39a] states that the incorporation of methane is very sensitive to the catalyst composition and the method of preparation and pretreatment, and that the inconsistency in the data from the different laboratories may be related to these factors.

COBALT CATALYSTS

Kinetics

In many respects the kinetics of the Fischer-Tropsch synthesis on cobalt and on nickel catalysts are similar. The hydrogen: carbon monoxide usage ratio varies from 2.1 to 2.2 over wide ranges of flow, temperature, gas composition, pressure, and catalyst composition.[33, 42, 43]

[40] S. R. Craxford, *Fuel*, **26**, 119 (1947).

[41] P. H. Emmett and J. T. Kummer, private communication.

[42] B. Seligman and R. B. Anderson, *Ind. Eng. Chem.*, to be published.

[43] S. Watanabe, K. Morikawa, and S. Igawa, *J. Soc. Chem. Ind. Japan*, **38**, Suppl. binding, 70 (1935).

Murata and Tsuneoka [44] studied the effect of variation of flow and weight of catalyst on the activity and selectivity of a Co:Ni:Si (100:100:200) skeletal-type catalyst. The conversion curves did not increase after 80–85 per cent of the reactants was converted, as shown in Figure 27, and the yield of "benzine" was approximately directly proportional to the conversion up to this point.

The variation of the extent of conversion with the reciprocal of space velocity for a standard Co-ThO_2-kieselguhr catalyst is somewhat similar

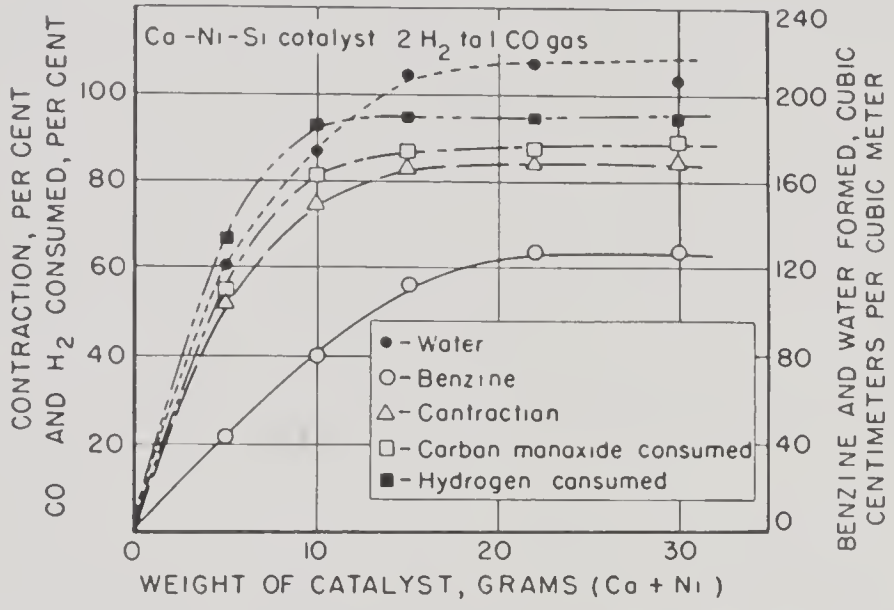


FIGURE 6–27. Variation of gas composition and conversion with weight of catalyst charge at constant flow of synthesis gas. Reproduced from reference 44.

to that observed on nickel catalysts, as shown in the data of Anderson, Krieg, Friedel, and Mason [45] in Figure 28. The percentage conversion increased uniformly as the space velocity was decreased. With $3.5H_2$:1CO gas the conversion curves were approximately linear, and they flattened out when 60–70 per cent of the carbon monoxide was consumed. With $2H_2$:1CO and $1H_2$:1CO gas the conversion plot was not linear; however, within the accuracy of the data, considerable portions of the curves could be represented by straight lines. Thus, the rate of synthesis was not greatly dependent upon the partial pressures of reactants and products, which varied considerably over the catalyst bed. This is shown in Figures 29, 30, and 31, in which the partial pressures of the reactants and products, the apparent contraction, and the liters of

[44] Y. Murata and S. Tsuneoka, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **30**, 40 (1935); Y. Murata, S. Ishikawa, and S. Tsuneoka, *ibid.*, **30**, 52 (1935).

[45] R. B. Anderson, A. Krieg, R. A. Friedel, and L. S. Mason, *Ind. Eng. Chem.*, **41**, 2,189 (1949).

gas consumed per hour are plotted as a function of bed length. These data represent a portion of those presented in Figure 28. The experiments with different gas compositions in Figures 28 and 31 were made

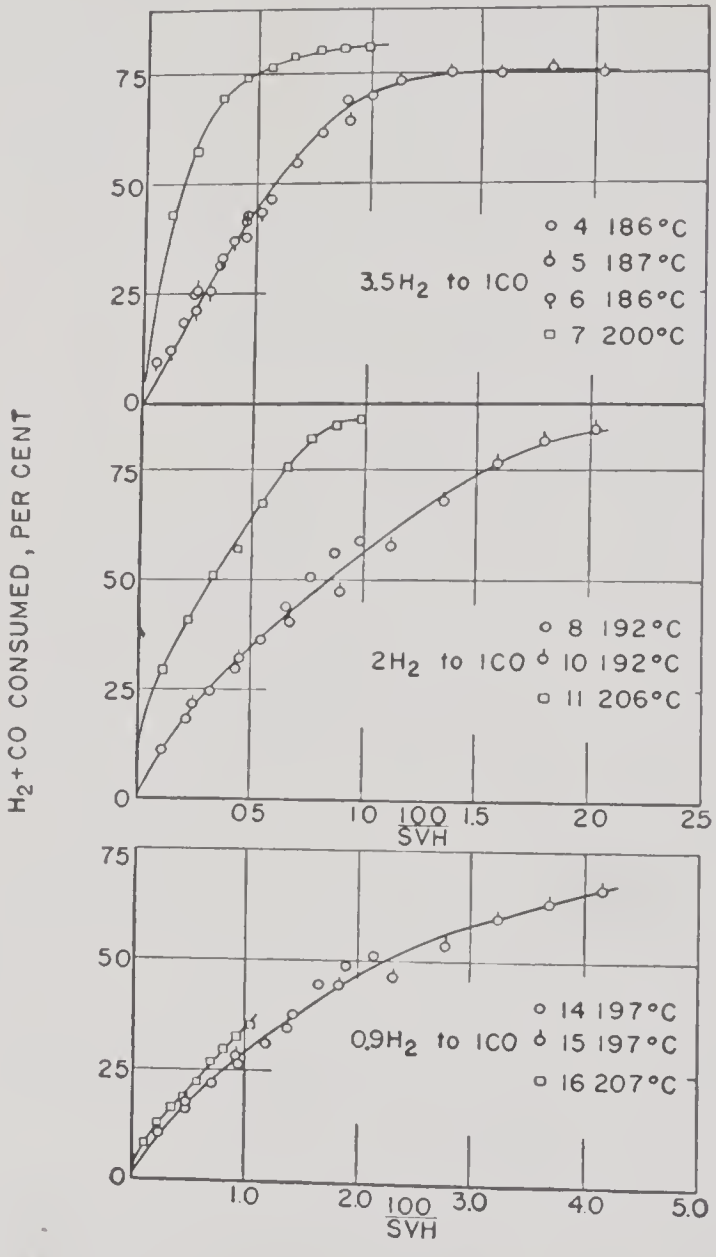


FIGURE 6–28. Variation of the extent of conversion of hydrogen plus carbon monoxide with the reciprocal of the space velocity for Co-ThO_2-kieselguhr catalyst at atmospheric pressure with synthesis gas having ratios of H_2:CO of 3.5, 2, and 0.9. Reproduced by permission from reference 45.

at different periods in the life of the catalyst, and thus should not be compared with respect to the influence of composition of synthesis gas on the rate of synthesis. The factors governing the formation of methane and carbon dioxide will be discussed later in this section.

Erosejev, Runtso, and Volkowa [46] found that the rate of synthesis on a cobalt-thoria-silica gel catalyst at atmospheric pressure and 200°C

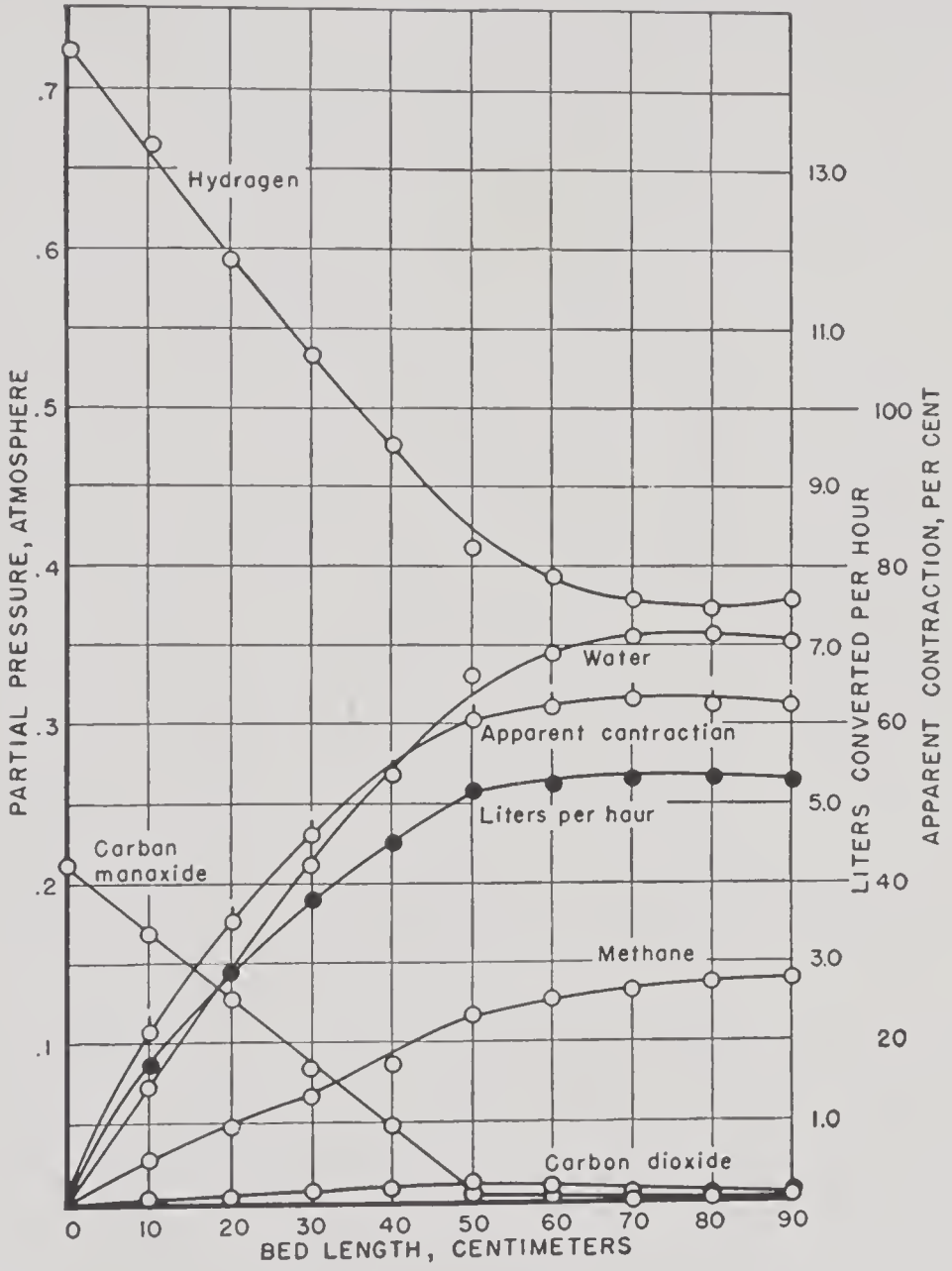


FIGURE 6–29. Test 5. A plot of partial pressures of reactants and products, apparent contractions, and integral reaction rate as a function of bed length for Co:ThO_2:-kieselguhr catalyst 108B with 3.42H_2 to 1CO gas at 187°C and space velocity of 49.3 per hour. Inflow was 0.0646 l (STP) per g of unreduced catalyst per hr. Reproduced by permission from reference 45.

varied linearly with the reciprocal of space velocity in the range of conversion of 25–45 per cent, as shown in Figure 32. This appears to be only a linear portion of the type of conversion curves shown in Figure 28.

[46] B. V. Erosejev, A. P. Runtso, and A. A. Volkowa, *Acta Physicochim. U.R.S.S.*, **13**, 111 (1940).

From Figures 28–31, it may be inferred that the rate of synthesis is not greatly dependent upon the total operating pressure. The rate of

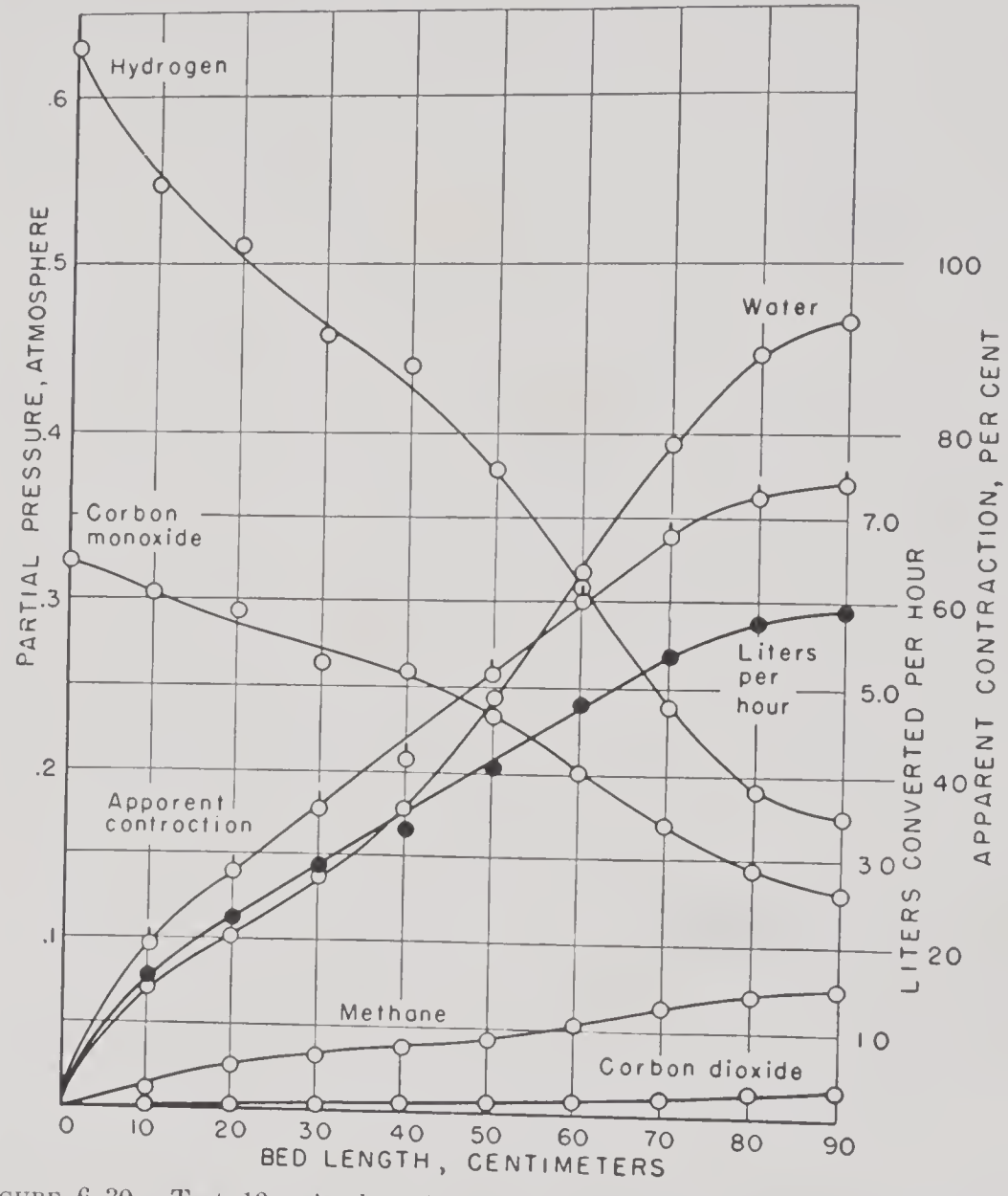


FIGURE 6–30. Test 10. A plot of partial pressures of reactants and products, apparent contractions, and integral reaction rate as a function of bed length for Co:ThO_2:kieselguhr catalyst 108B with 1.96H_2 to 1CO gas at 192°C and space velocity of 49.5 per hour. Inflow was 0.065 l (STP) per g of unreduced catalyst per hr. Reproduced by permission from reference 45.

synthesis above atmospheric pressure was virtually independent of operating pressure on cobalt catalysts supported on kieselguhr [13] but was decreased by pressure on other types of cobalt catalysts.[47] At pressures less than atmospheric the rate of synthesis was dependent upon total

[47] F. Fischer and H. Pichler, *Brennstoff-Chem.*, **12**, 365 (1931).

pressure. Fischer and Pichler found that, at the same temperature, the contraction observed at atmospheric pressure and a given space velocity was obtained at $\frac{1}{3}$ atm when the space velocity was decreased to $\frac{1}{3}$. This

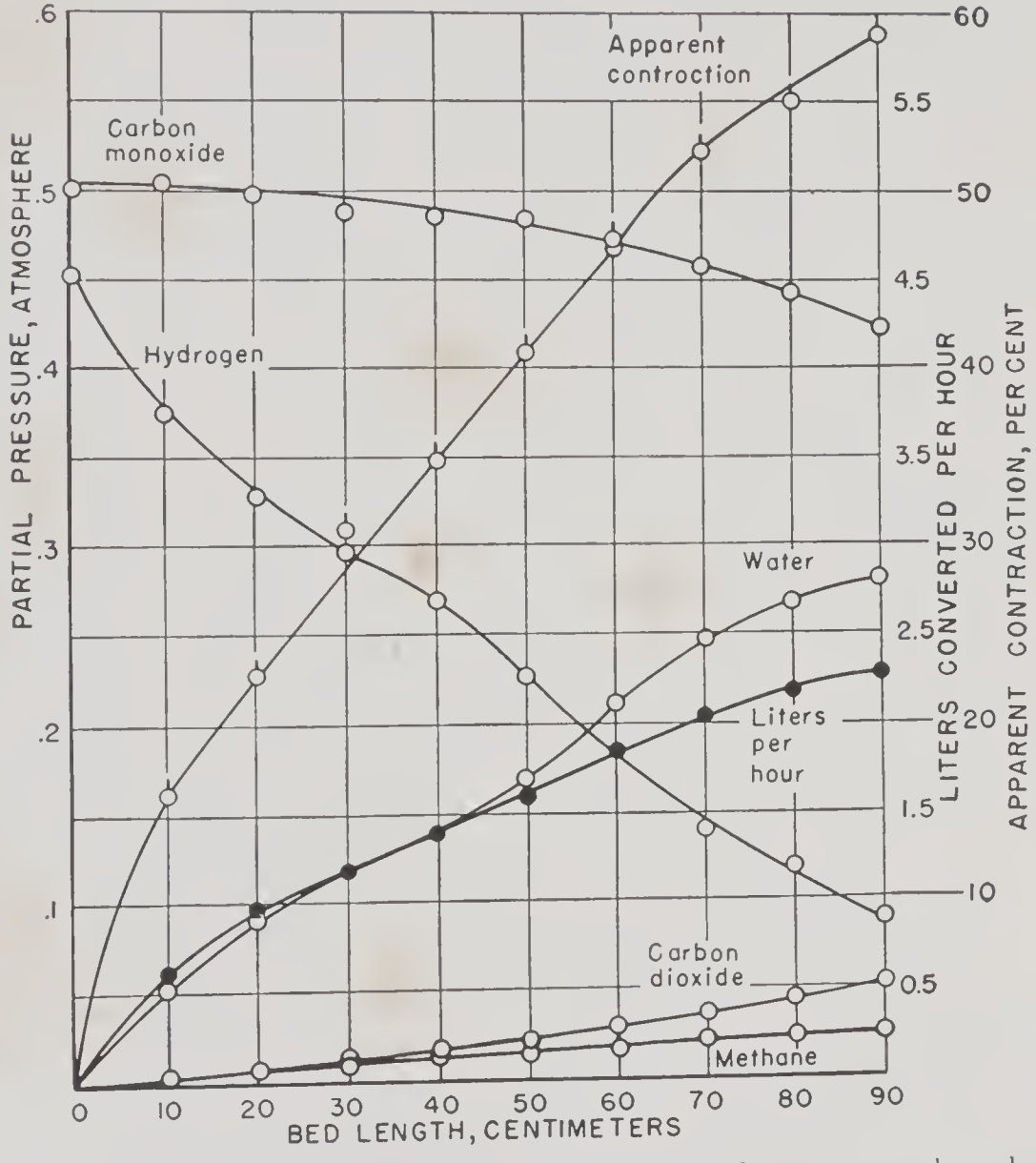


FIGURE 6–31. Test 15. A plot of partial pressures of reactants and products, apparent contractions, and integral reaction rate as a function of bed length for Co:ThO_2:kieselguhr catalyst 108B with 0.90H_2 to 1CO gas at 197°C and space velocity of 24.1 per hour. Inflow was 0.0316 l (STP) per g of unreduced catalyst per hr. Reproduced by permission from reference 45.

suggests that in this range of pressure the rate was proportional to total pressure. Weller [48] found that the rate of synthesis on a cobalt-thoria-kieselguhr catalyst varied with the total pressure to the 0.45 power, from 0.4 to 0.9 atm. However, Ruhrchemie tests [49] of a cobalt-thoria-

[48] S. Weller, in H. H. Storch *et al.*, *U. S. Bur. Mines Tech. Paper* 709 (1948), p 44.
[49] T.O.M. Reel 36, Bag 3,451, Item 13.

magnesia-kieselguhr catalyst described in Table 3 of Chapter 4 indicate that the rate of synthesis was constant from 0.2 to 7.0 atm. Thus, there appears to be some uncertainty as to the pressure below which the rate begins to decrease. This difference may be related to the partial pressure of products in the gas phase, since the experiments of Weller were made

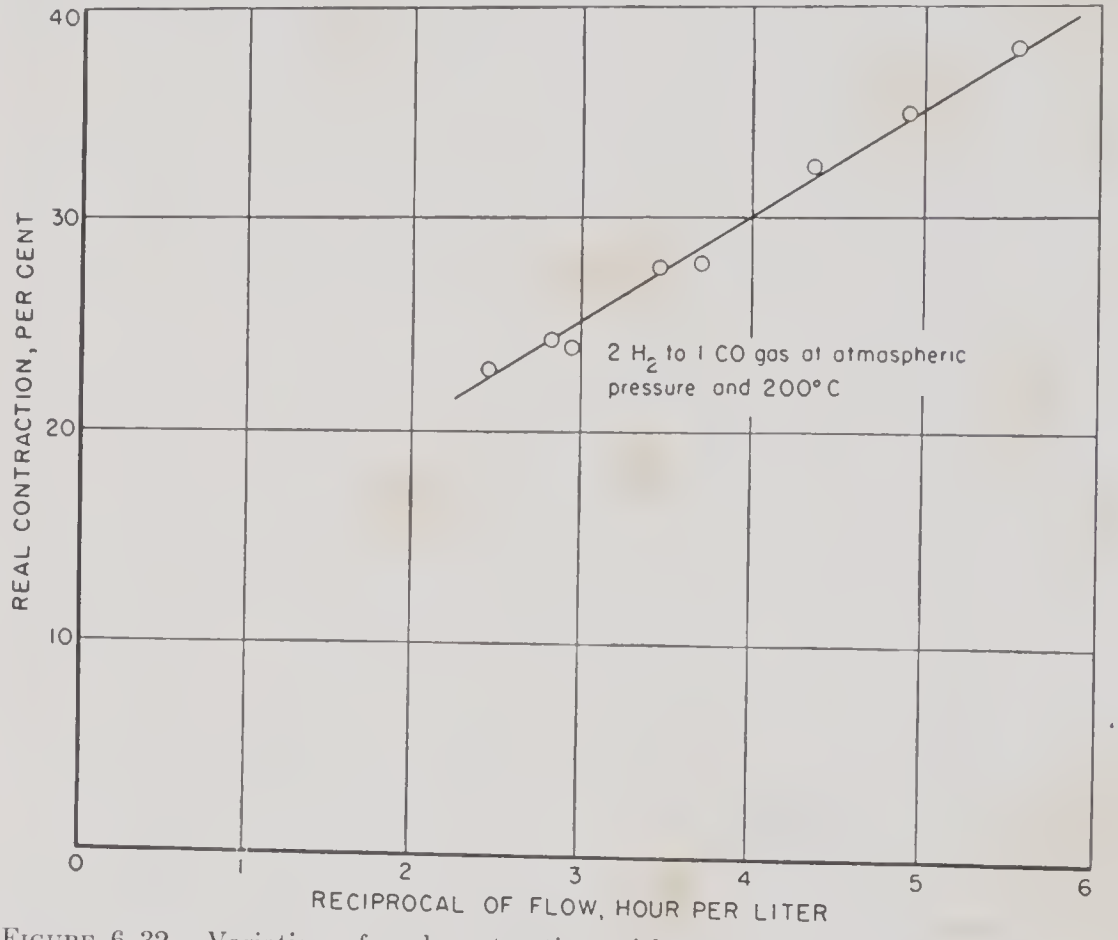


FIGURE 6–32. Variation of real contraction with reciprocal of flow on a cobalt-thoria-silica gel catalyst. Reproduced from data of reference 46.

at high flows with conversions of 1–2 per cent, whereas the Ruhrchemie tests were made at low space velocities and about 60 per cent conversion. At pressures above 30 atm, the activity decreased rapidly, probably because of carbonyl corrosion.[50]

At atmospheric pressure with $2H_2:1CO$ or gases containing larger fractions of hydrogen, cobalt catalysts remained active for 10 or more days, but with $1H_2:1CO$ gas the activity decreased more rapidly. However, in the medium-pressure range, the activity remained relatively constant for periods of several months with all gas mixtures.

In a static system, Craxford and Rideal [30] found that the rate of synthesis on a cobalt catalyst at constant temperature was at a maximum

[50] F. Fischer and H. Pichler, *Brennstoff-Chem.*, **20**, 41 (1939).

for a gas containing about $2H_2:1CO$. Seligman [42] studied the influence of gas composition on the rate of synthesis on a Co-ThO_2-kieselguhr catalyst at constant temperature and flow of synthesis gas. The extent of conversion varied from 10 to 20 per cent, so that neither of the reactants was completely consumed. The volumes of hydrogen plus carbon monoxide consumed per hour were 23.6, 24.6, and 17.7 cc (STP)

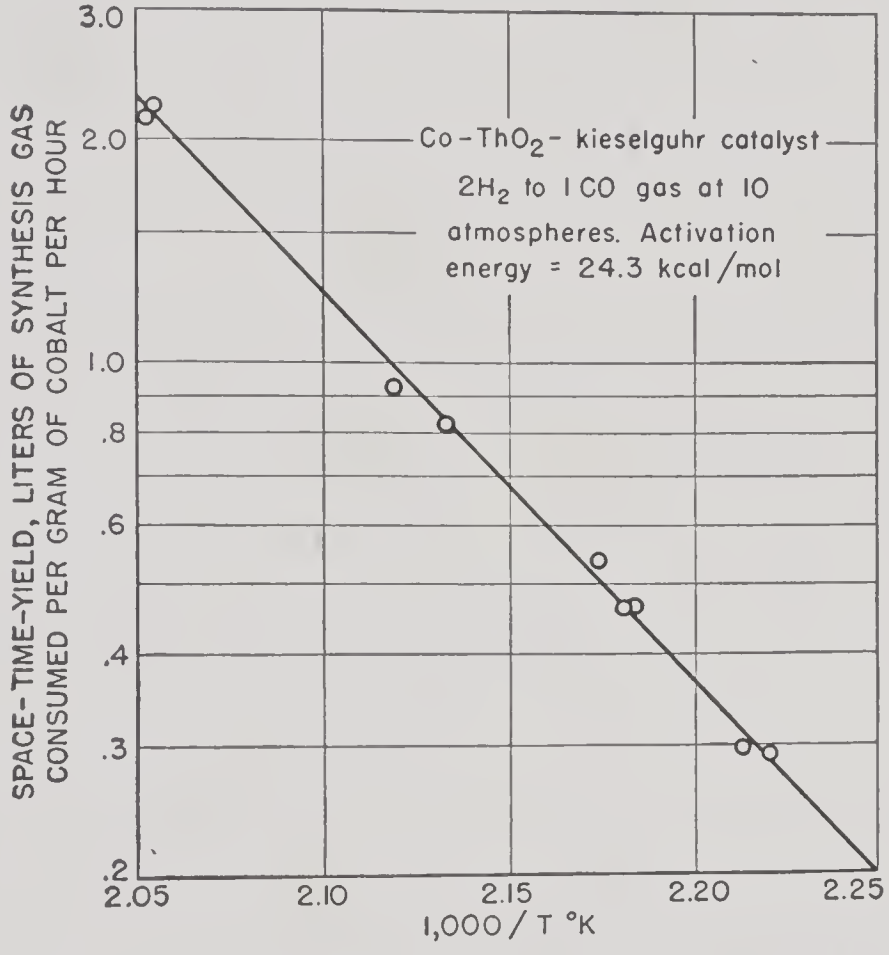


FIGURE 6–33. Variation of space-time-yield with temperature. Data are for the first stage of a two-stage operation. Constructed from data of reference 51.

per g of catalyst at 170°C for $3H_2:1CO$, $2H_2:1CO$, and $1H_2:1CO$ gases, respectively.

The effect of diluents on conversion has been discussed in Chapter 4, pp 329–336. Tentative conclusions about the effect of diluents may be summarized as follows: (*a*) In tests at constant total flow of synthesis gas plus diluent, the percentage conversion of the synthesis gas increased, but the space-time-yield of the reaction decreased with increasing amounts of diluent. (*b*) In tests at constant flow of synthesis gas both the percentage conversion and space-time-yield decreased with increasing amounts of diluent.

The rate of synthesis is strongly dependent upon temperature. The variation of rate with temperature on a Co-ThO_2-MgO-kieselguhr cata-

lyst with $2H_2$:1CO gas at atmospheric pressure was studied in a flowing system by Anderson, Krieg, Seligman, and O'Neill.[33] The flow of gas and temperature were varied to maintain the percentage conversion approximately constant, and apparent activation energies were computed from the space-time-yields and temperatures at constant percentage conversion. For constant percentage conversions varying from 15 to 75 per cent, apparent activation energies of 25 ± 1 kcal per mole were

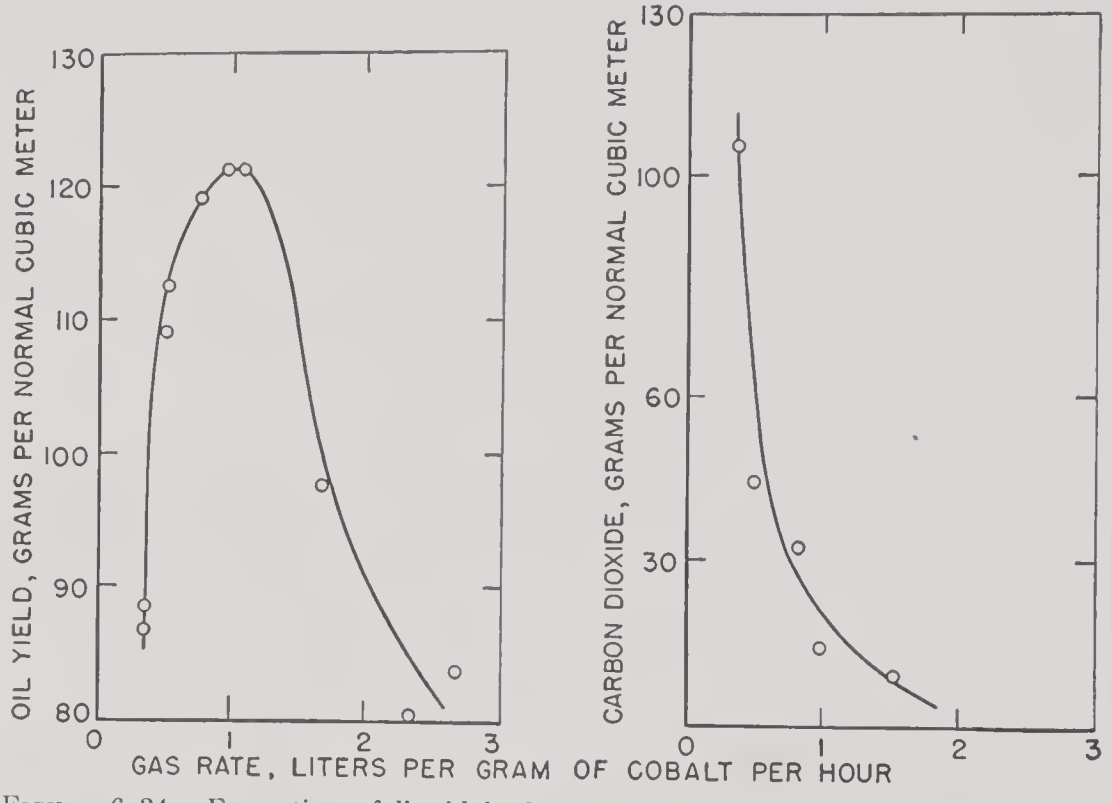


FIGURE 6–34. Formation of liquid hydrocarbons and carbon dioxide with a Co-ThO_2-MgO-kieselguhr catalyst with $2H_2$ to 1CO gas at 185°C as a function of flow rate. Reproduced by permission from reference 52.

found. Weller [32] found similar activation energies for a Co-ThO_2-kieselguhr catalyst at atmospheric pressure with $2H_2$:1CO gas at high space velocities and low conversions (1–2 per cent). At 7.8 atm, Seligman [42] found an activation energy of 20.0 kcal per mole for a Co-ThO_2-MgO-kieselguhr catalyst with $2H_2$:1CO gas. An activation energy of 24.3 kcal per mole was computed from the first stage of a two-stage test of Fischer and Pichler [51] with a Co-ThO_2-kieselguhr catalyst with $2H_2$:1CO gas at 10 atm. A plot of these data according to the Arrhenius equation is given in Figure 33.

Results of Craxford [52] on the formation of liquid hydrocarbons and carbon dioxide on a Co-ThO_2-MgO-kieselguhr catalyst with $2H_2$:1CO

[51] F. Fischer and H. Pichler, *ibid.*, **20**, 221 (1939).

[52] S. R. Craxford, *Trans. Faraday Soc.*, **42**, 576 (1946).

gas at atmospheric pressure and 185°C are presented in Figure 34. The synthesis gas was probably fairly completely consumed at a flow of 1 l per g per hr. At lower flows the yield of liquid hydrocarbons decreased, and the yield of carbon dioxide increased. Craxford postulated that hydrocracking of liquid hydrocarbon and the water-gas reaction occurred in the portion of the catalyst bed not actively engaged in the synthesis. The surface of this portion of the catalyst was postulated to consist of cobalt atoms, as compared with cobalt carbide for the catalyst surface engaged in the synthesis. Previously, Watanabe, Morikawa, and Igawa [43] observed that the yields of liquid products per cubic meter passed through a maximum as the space velocity was decreased, as shown in Table 14. The space-time-yield increased with increasing space velocity.

Table 14. Variation of Yield with Space Velocity with a Co-Cu-ThO_2 Catalyst at Atmospheric Pressure [a]

(Temperature = 197°C.)

Space Velocity	Contraction, per cent	Yield		Space-Time-Yield of Liquid Hydrocarbons, mg per hr
		Water, g per cu m	Liquid Hydrocarbons, g per cu m	
105	83.5	195	92	76
147	82.9	193	109	123
226	71.9	169	78	136
320	55.3	134	56	138

[a] S. Watanabe, K. Morikawa, and S. Igawa; see reference 43.

Koelbel and Engelhardt [53] studied the production of water and carbon dioxide on a cobalt-thoria-kieselguhr catalyst. With $2H_2:1CO$ gas at 180°C the space velocity was decreased from 100 to 10, and the production of CO_2 increased about twenty-fold. Thus, at a space velocity of 10 with gases containing ratios of $H_2:CO$ of 1.8, 1.1, 0.8, and 0.6, the percentages of the synthesis proceeding by reactions that eventually produced carbon dioxide were 19, 51, 77, and 99 per cent, respectively. These workers concluded that carbon dioxide was produced by a secondary water-gas reaction which was favored by high partial pressures of carbon monoxide and water vapor. These data cannot be adequately explained by Craxford's carbide theory. The water-gas reaction was studied by Koelbel and Engelhardt with mixtures of $1CO:1H_2O$ at 240°C, and it was found that the reduced catalyst was more active in the water-gas reaction than a catalyst used for one day in the synthesis; a

[53] H. Koelbel and F. Engelhardt, *Erdöl u. Kohle*, **2**, 52 (1949).

catalyst converted to cobalt carbide by carbon monoxide treatment at 270°C had a considerably lower activity than the used catalyst. A catalyst used in synthesis for 100 hr was studied in the water-gas reaction with $1CO:1H_2O$ gas at various temperatures, as shown in Figure 35. The water-gas reaction was not rapid in the range of temperatures normally used with cobalt catalysts, *ie*, 180°–200°C.

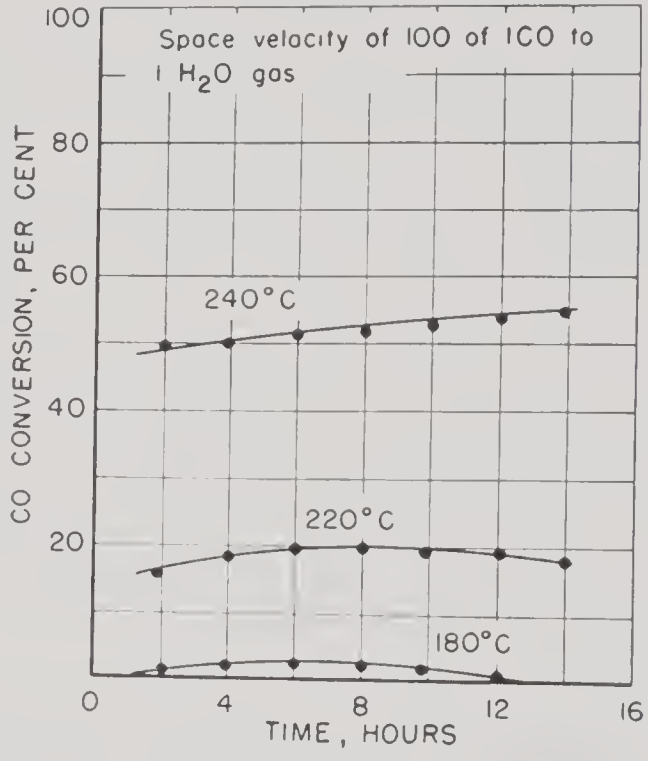


FIGURE 6–35. Conversion of carbon monoxide in a mixture of carbon monoxide and water vapor on a used cobalt catalyst as a function of temperature. Reproduced by permission from reference 53.

Anderson, Krieg, Friedel, and Mason [45] determined the production of methane and carbon dioxide as a function of bed length with a Co-ThO_2-kieselguhr catalyst, at atmospheric pressure. The yields of methane, expressed as grams of methane produced per cubic meter of hydrogen plus carbon monoxide consumed in each interval of the catalyst bed, are plotted against bed length in Figures 36, 37, and 38. With $2H_2:1CO$ gas (Figure 36) the differential production of methane was high in the first part of the bed, passed through a minimum, and increased at the exit end of the bed. With $3H_2:1CO$ gas (Figure 37) the yield of methane increased throughout the bed, exceeding 179 g per cu m of hydrogen plus carbon monoxide consumed in tests 5 and 7. A yield of 179 g per cu m is the highest one possible for hydrogenation of oxides of carbon by the reaction, $3H_2 + CO = CH_4 + H_2O$ or $4H_2 + CO_2 = CH_4 + 2H_2O$. Since the methane yield exceeded 179 g per cu m, at least

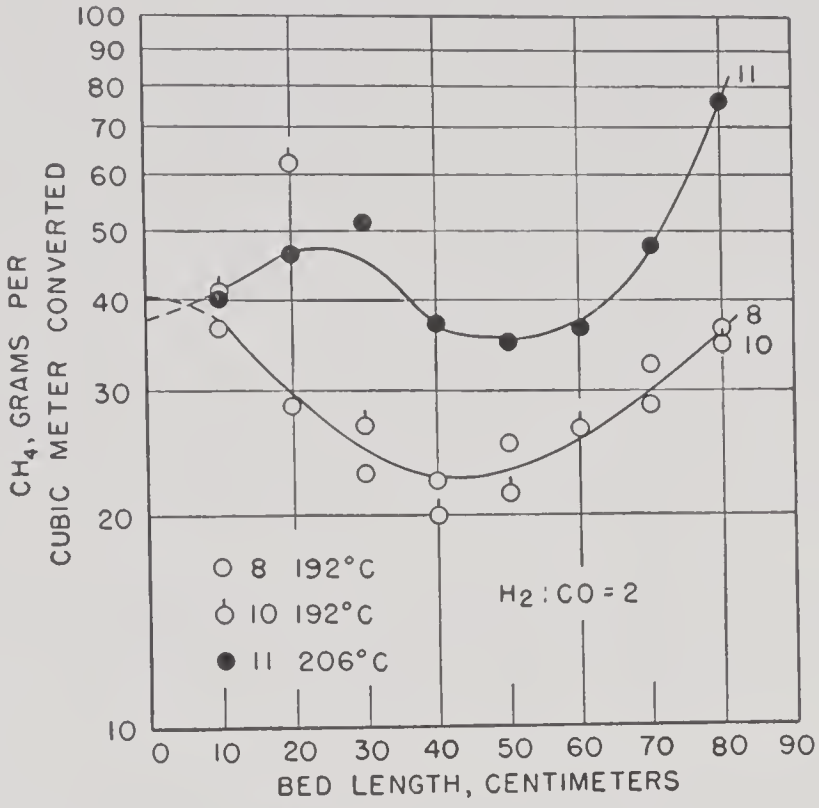


FIGURE 6–36. Differential formation of methane-bed length curves for tests 8, 10, and 11 with $2H_2$ to 1CO gas. The methane yields are expressed in grams per cubic meter of H_2 plus CO consumed. Reproduced by permission from reference 45.

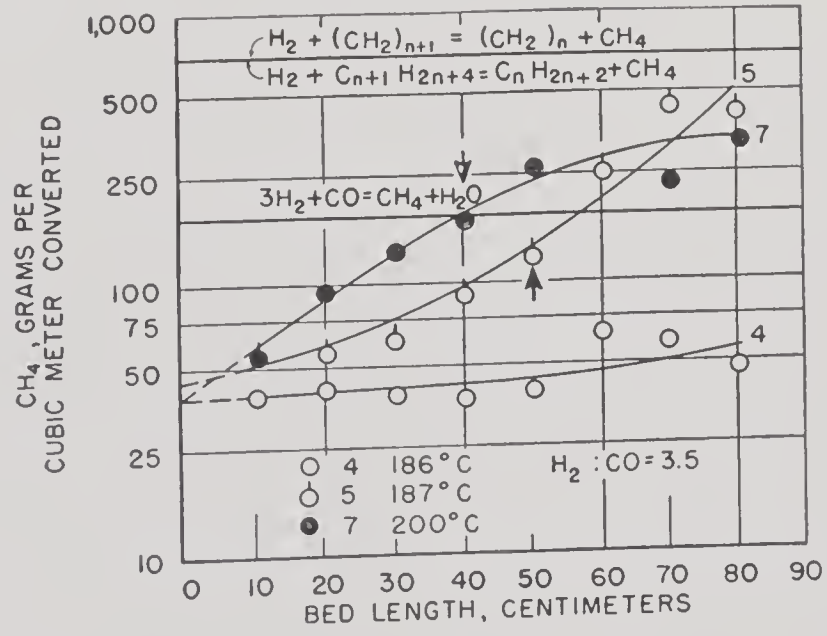


FIGURE 6–37. Differential formation of methane-bed length curves for tests 4, 5, and 7 with $3.5H_2$ to 1CO gas. The methane yields are expressed in grams per cubic meter of H_2 plus CO consumed. The arrows indicate the position within the bed where the pressure of carbon monoxide had decreased below 0.01 atm. Reproduced by permission from reference 45.

part of it must be formed by hydrocracking, as postulated by Craxford.[52] With $1H_2:1CO$ gas (Figure 38) the differential yields of methane were lower than in tests with gas containing more hydrogen, and the methane yields either remained constant or decreased with length of catalyst bed. The methane curves have been extrapolated to zero bed length. Although there is considerable uncertainty in this extrapolation, the extended curves indicate that at least part of the methane is formed by

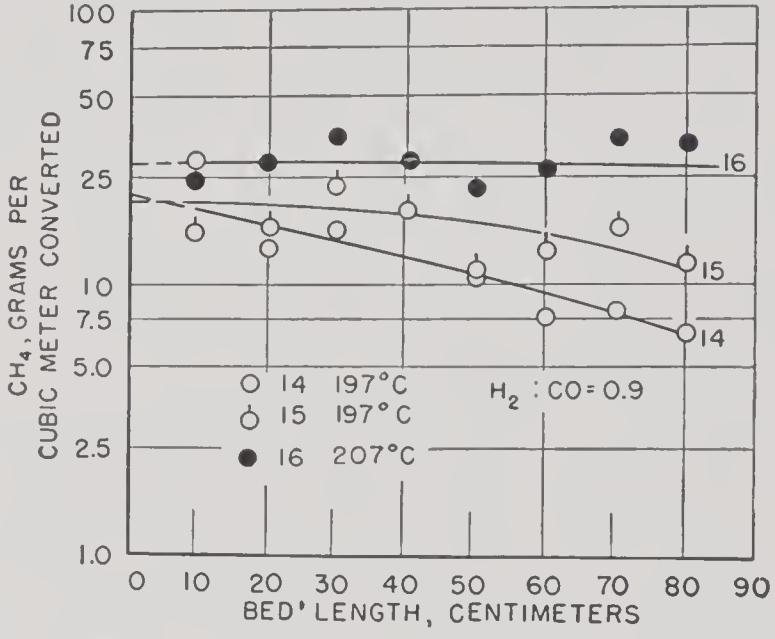


FIGURE 6–38. Differential formation of methane-bed length curves for tests 14, 15, and 16 with $0.9H_2$ to 1CO gas. The methane yields are expressed in grams per cubic meter of H_2 plus CO consumed. Reproduced by permission from reference 45.

primary processes. The production of methane increased with increasing partial pressures of hydrogen and hydrocarbon products. An increase in temperature increased the yield of methane.

The yields of carbon dioxide, expressed as grams of carbon dioxide per cubic meter of carbon monoxide consumed in each interval of the bed, are plotted against bed length in Figures 39, 40, and 41. This definition of carbon dioxide formation was necessary, since no change occurs in the number of moles of hydrogen plus carbon monoxide in the water-gas reaction. In all three figures, the yields of carbon dioxide increased with bed length, *ie*, with increasing partial pressure of water vapor. In experiment 11 of Figure 39 the yield of carbon dioxide exceeded the highest possible value for hydrogenation reactions. With $3.5H_2:1CO$ gas (Figure 40) carbon dioxide was formed in sizable amounts until all the carbon monoxide had been consumed. Beyond this point, as indicated by arrows, carbon dioxide was consumed, presumably by hydrogenation, since the partial pressures in the gas stream were such that the reverse

of the water-gas reaction should not occur. Chiefly methane was produced in this portion of the bed (Figure 37). For equal percentage conversion, *ie*, equal partial pressures of water vapor, the production of carbon dioxide was greater for gases containing higher partial pressures of carbon monoxide. Thus, the production of carbon dioxide was

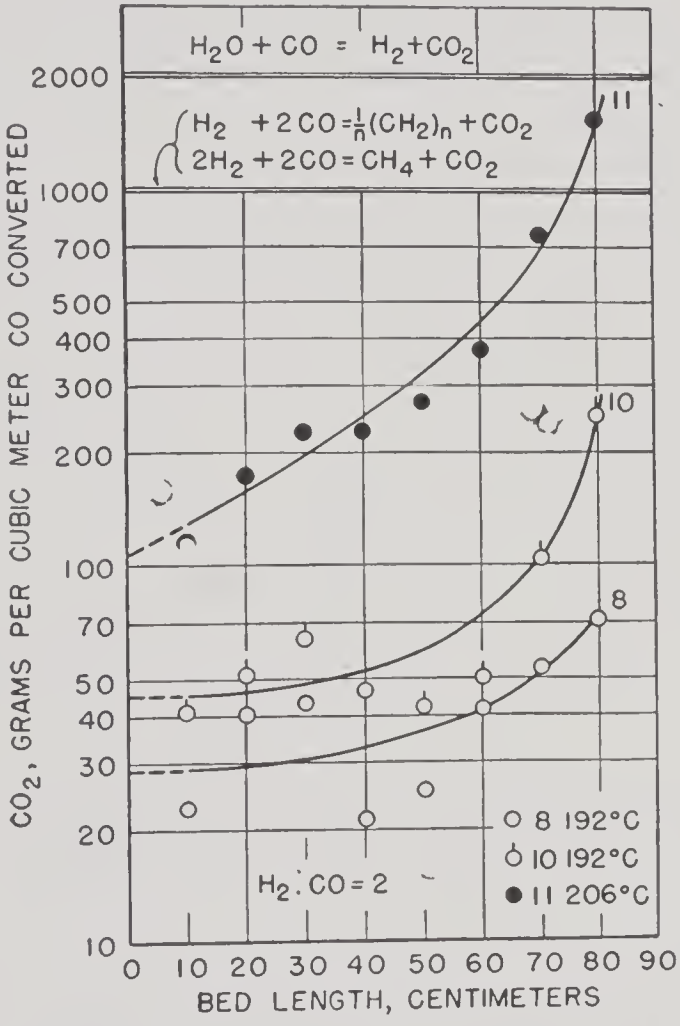


FIGURE 6–39. Differential formation of carbon dioxide-bed length curves for tests 8, 10, and 11 with $2H_2$ to 1CO gas. The carbon dioxide yields are expressed as grams per cubic meter of carbon monoxide consumed. Reproduced by permission from reference 45.

favored by high partial pressures of water vapor and carbon monoxide. Extension of the carbon dioxide curves to zero bed length indicated that at least part of the carbon dioxide was produced by primary processes.

To summarize these data, methane and carbon dioxide were produced throughout the catalyst bed, at least in part by primary processes. Methane, which was also produced by hydrocracking, was favored by high partial pressures of hydrogen and hydrocarbon products or possibly high ratios of the partial pressures of these substances to the partial pressure of carbon monoxide. At least part of the carbon dioxide was

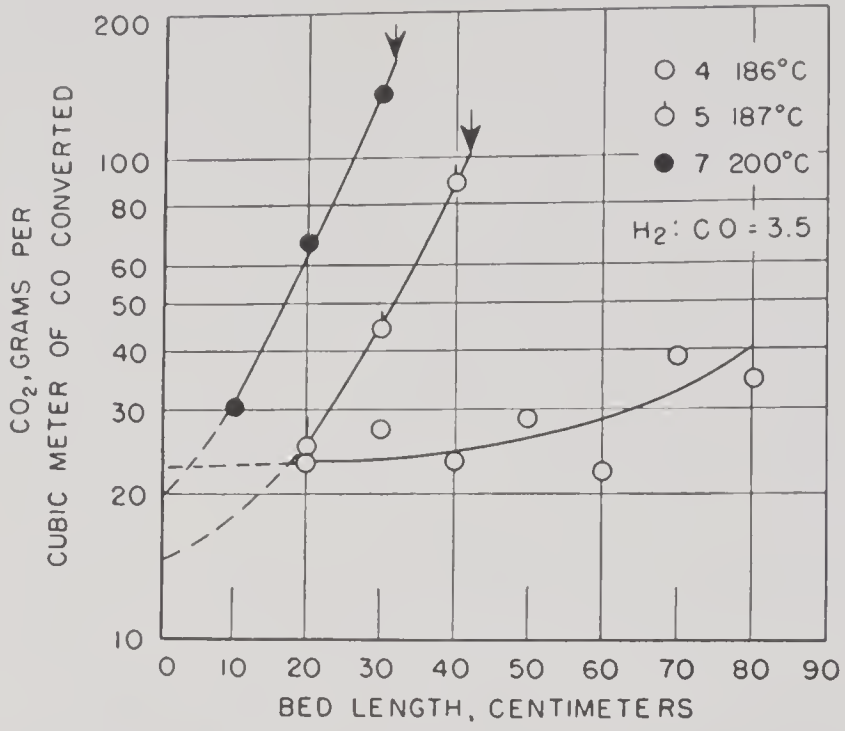


FIGURE 6–40. Differential formation of carbon dioxide-bed length curves for tests 4, 5, and 7 with $3.5H_2$ to 1CO gas. The carbon dioxide yields are expressed as grams per cubic meter of carbon monoxide consumed. The arrows indicate the position within the bed where the pressure of carbon monoxide had decreased below 0.01 atm. Beyond these points in the bed carbon dioxide was consumed. Reproduced by permission from reference 45.

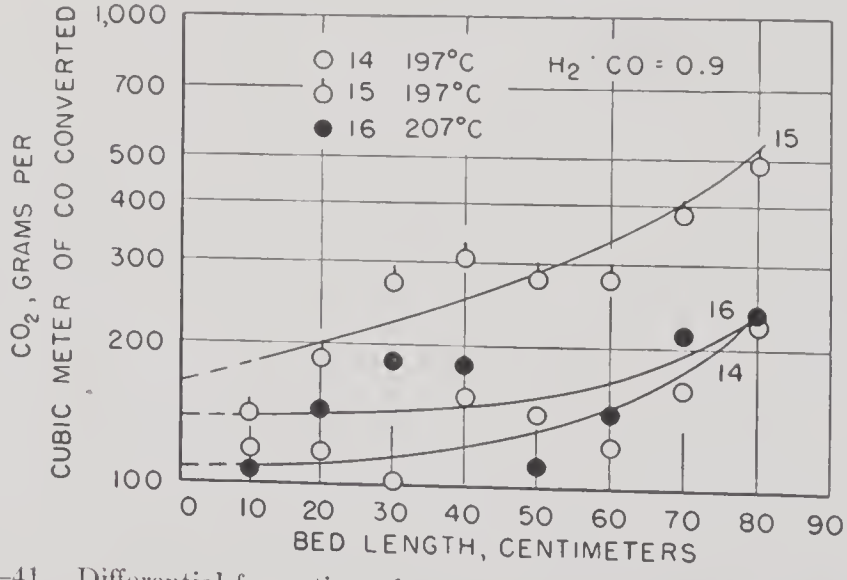


FIGURE 6–41. Differential formation of carbon dioxide-bed length curves for tests 14, 15, and 16 with $0.9H_2$ to 1CO gas. The carbon dioxide yields are expressed as grams per cubic meter of carbon monoxide consumed. Reproduced by permission from reference 45.

produced by a secondary water-gas reaction; carbon dioxide production was favored by high partial pressures of water vapor and carbon monoxide or possibly high ratios of these constituents to the partial pressure of hydrogen. When the carbon monoxide had been almost completely consumed, the carbon dioxide was hydrogenated. This observation agrees with experiments of Fischer and Pichler [54, 55] in which carbon dioxide was not hydrogenated in the presence of carbon monoxide. The carbide theory of Craxford [30, 52] does not appear to explain satisfactorily methane and carbon dioxide production. The experiments involving the incorporation of methane (p 504) neither confirm nor deny the carbide theory, but these data may support the polymerization-depolymerization mechanism advanced by Craxford.[30]

Physical and Chemical Nature of Used Cobalt Catalysts

In the synthesis, the pores of cobalt catalysts are at least partially filled with hydrocarbons that are probably liquid at synthesis temperatures. Surface area, density, and pore volume studies of a Co-ThO_2-MgO-kieselguhr catalyst after use in the synthesis and after hydrogen treatment are reported in Tables 15 and 16. The catalyst was used in the synthesis with $2H_2$:1CO gas at atmospheric pressure for 11 weeks, with hydrogen reactivation at 200°C after each weekly period. After 4 days of operation in the twelfth week, the catalyst was removed from the converter and transferred in an inert atmosphere to suitable adsorption and density tubes.

The data in Table 15 show that after use in the synthesis the area of the catalyst was only 5.4 per cent of that observed after the initial reduction. Mild hydrogen reactivation at 200°C restored the surface area to 91.8 per cent of the value for the catalyst in its original, reduced state. Subsequent reduction at 400°C under the conditions used for the initial reduction of the catalyst almost restored the surface area to the initial value in the reduced state. The ratio of volume of chemisorbed carbon monoxide (V_{CO}) to physically adsorbed nitrogen (V_m) varied from 0.13 to 0.21. The ratio increased with increasing surface area of the sample. After use in synthesis, the helium density and pore volume (volume of pores with openings smaller than 5 microns in diameter; see p 50, Chapter 2) were much lower and the mercury density was higher than the corresponding values in the original, reduced catalyst. After reduction at 400°C, these values were nearly restored. Thus, the surface area, densities, and pore volume of the used catalyst after re-

[54] F. Fischer and H. Pichler, *Brennstoff-Chem.*, **14**, 306 (1933).

[55] H. Pichler, *ibid.*, **24**, 39 (1943).

TABLE 15. ADSORPTION DATA FOR REDUCED AND USED COBALT CATALYST 89FF [a,b]

(All adsorption data per gram of unreduced catalyst.)

Treatment	Cumulative Weight Loss,[c] per cent	Surface Area, sq m per g	V_m,[d] cc per g	V_{CO},[e] cc per g	$\frac{V_{CO}}{V_m}$
a. Reduced 2 hr, H_2 at 400°C, SVH = 6,000 [f]	....	80.8	18.45	3.2	0.173
b. Used:					
(*a*) plus 12 weeks of synthesis	0.0	4.36	1.00	0.13	0.130
c. (*b*) plus 2 hr of H_2 at 200°C, SVH = 200	23.5	70.5	16.1	2.7	0.168
d. (*c*) plus 20 hr of H_2 at 200°C, SVH = 200	23.7	74.2	16.9	3.2	0.189
e. (*d*) plus 2 hr of H_2 at 400°C, SVH = 6,000	25.3	79.1	18.1	3.8	0.210

[a] Cobalt:thoria:magnesia:kieselguhr = 100:6:12:200.
[b] R. B. Anderson, W. K. Hall, A. Krieg, and B. Seligman; see reference 13.
[c] Weight based on weight of used catalyst as removed from converter.
[d] Volume of nitrogen corresponding to a physically adsorbed monolayer, cc (STP).
[e] Volume of carbon monoxide chemisorbed at −195°C, cc (STP).
[f] Space velocity per hr, volumes of gas (STP) per volume of catalyst per hr.

TABLE 16. DENSITY AND PORE VOLUME DATA ON REDUCED AND USED COBALT CATALYST 89FF [a,b]

Treatment	Cumulative Weight Loss,[c] per cent	d_{He}, g per cc	d_{Hg}, g per cc	Pore Volume, cc per g
a. Reduced 2 hr at H_2 at 400°C, SVH [d] = 6,000	....	3.031	1.138	0.549 [e]
b. Used: (*a*) plus 12 weeks of synthesis	0.0	1.891	1.471	0.151 [f] (0.201) [e]
c. (*b*) plus 2 hr of H_2 at 200°C, SVH = 200	23.8	2.881	.....	.....
d. (*c*) plus 2 hr of H_2 at 400°C, SVH = 6,000	25.5	3.007	1.112	0.566 [e]

[a] Cobalt:thoria:magnesia:kieselguhr = 100:6:12:200.
[b] R. B. Anderson, W. K. Hall, A. Krieg, and B. Seligman; see reference 13.
[c] Weight was based on weight of used catalyst as removed from converter. These values were obtained with a different portion of used catalyst from that in Table 15.
[d] Space velocity per hr, volumes of gas (STP) per volume of catalyst per hr.
[e] Pore volume, cc per g of reduced catalyst.
[f] Pore volume, cc per g of catalyst as removed from converter.

reduction at 400°C were nearly identical with those of the original reduced catalyst. Thus, the catalyst had not sintered or disintegrated to an appreciable extent in 11 weeks of testing.

The volumes of mercury displaced by the used catalyst before and after hydrogenation, per unit weight of cobalt, were identical, indicating that the adsorbed hydrocarbons were located within the pellet in the space not penetrated by mercury and not on the external surface of the catalyst. At 30°C, 65 per cent of the pore volume of the used catalyst was filled with hydrocarbons. Since it is probable that the density of this wax did not decrease more than 25 per cent on being heated to 183°C, and that the density of the catalyst changed by a considerably smaller amount, about 80 per cent of the pore volume was probably filled at 183°C. The hydrocarbons removed by hydrogenation had a density of 0.90, as calculated from change in weight and change in volume of helium displaced. This value was in agreement with the densities of soft and hard paraffins from atmospheric-pressure synthesis, 0.90 and 0.93, respectively, as reported by Pichler.[23]

The data in Tables 15 and 16 show definitely that the catalyst surface in its normal condition of operation at atmospheric pressure is heavily covered with hydrocarbons. At atmospheric pressure, the rate of synthesis as a function of time is characterized by a short initial period of high activity, a longer period of 2 or more weeks at a somewhat lower, relatively constant activity, and finally a short period of decreasing activity at the end of which reactivation is necessary.[56] Craxford [52] suggests that this final rapid loss in activity occurs when the pores become completely filled with wax.

In pressure operation, the catalyst is believed to be completely filled with hydrocarbon product at all times.[52] Experimental data given in Table 17 indicate that the activities [57] of pelleted cobalt catalysts at an operating pressure of 1 atm are equal to or slightly greater than at 7.8 atm. Pelleted catalysts produced greater percentages of methane and light hydrocarbons at 7.8 atm than at 1 atm, but for granular catalysts the product distribution was the same under both conditions.

Table 18 presents data for a test of a pelleted catalyst operated alternately at 1 and 7.8 atm. The data show that the activity of the catalyst at 7.8 atm, as indicated by the synthesis temperature, was essentially the same as it was during each previous period at atmospheric pressure. However, the activity in each period at atmospheric pressure

[56] C. C. Hall and S. L. Smith, *J. Soc. Chem. Ind. (London)*, **65**, 128 (1946).

[57] In Tables 17 and 18, the space velocity of synthesis gas was constant and the temperature was varied to maintain a 70 per cent contraction. Thus, the lower temperature of operation corresponds to the greater activity.

TABLE 17. EFFECT OF OPERATING PRESSURE ON COBALT CATALYSTS [a]

(Tests at space velocity per hr of 100.)

Test	Operating Periods	Pressure, atm	Average Temperature,[b] °C	Apparent Contraction,[c] per cent	Products, per cent			
					CH_4	$C_3 + C_4$	C_1–C_4	Liquids and Solids
Pelleted [d] Co-ThO_2-kieselguhr catalyst 108B								
X-29	*b–g*	1	185 (186)	70.9	12.1	10.0	24.5	75.5
X-29	*i–p*	7.8	189 (186)	71.3	19.0	10.9	33.5	66.5
X-31	*b–j*	7.8	187	71.8	18.6	10.5	32.0	68.0
Granular [e] Co-ThO_2-MgO-kieselguhr catalyst 89K								
X-17	*b–k*	1	186 (187)	74.4	13.1	10.2	25.6	74.4
X-17	*v–d*	7.8	188 (188)	72.0	14.0	8.6	23.2	76.8
Pelleted [f] Co-ThO_2-MgO-kieselguhr catalyst 89J								
X-21	*c–l*	1	186 (186)	72.0	15.6	8.1	24.9	76.1
X-21	*o–u*	7.8	191 (188)	69.5	18.2	10.4	28.3	71.7

[a] R. B. Anderson, W. K. Hall, A. Krieg, and B. Seligman; see reference 13.

[b] The temperatures in parentheses are for the last 2 weeks of operation at 1 atm and the first 2 weeks of operation at 7.8 atm.

[c] Apparent contraction computed by $100(1 - V_E/V_I)$, where V_E is the flow of exit gas and V_I the flow of synthesis gas.

[d] Cylindrical pellets, 3.2 mm in diameter by 3.2 mm in length.
Broken filter cake.

[f] Cylindrical pellets, 3.2 mm in diameter by 1.6 mm in length.

was lower than it was in the previous period at 7.8 atm. Thus, operation at 7.8 atm decreased the activity in subsequent periods at atmospheric pressure. When hydrogen reactivation was omitted, this decrease in activity was greater than when hydrogen treatment was done.

In addition to changes in activity, an increase in the yields of methane and light hydrocarbons was observed. Apparently, these differences in activity are related to the effect of the amount and nature of adsorbed

TABLE 18. ALTERNATE OPERATION AT 1 AND 7.8 ATM OF PELLETED Co-ThO_2-KIESELGUHR CATALYST 108B [a]

(Operating periods were 5 or 6 days, hourly space velocity was 100.)

Operating Periods	Pressure, atm	Average Temperature, °C	Apparent Contraction,[b] per cent	Products, per cent			
				CH_4	$C_3 + C_4$	C_1–C_4	Liquids and Solids
e [c]	1	187	72.1	14.9	10.8	31.9	68.0
f [c]	1	186	70.1	15.4	16.5	34.0	66.0
g [c]	7.8	186	67.2	21.0	13.0	34.9	65.1
h [c]	1	191	70.3	19.2	10.0	36.4	63.6
i [c]	7.8	188	69.9	24.6	13.4	42.5	57.5
j	1	198	69.1	....	....	....	....
k [c]	7.8	198	71.3	41.4	10.3	53.6	46.4
l	1	207	68.7	24.6 [d]	....	....	....

[a] R. B. Anderson, W. K. Hall, A. Krieg, and B. Seligman; see reference 13.

[b] See note *c* of Table 17.

[c] A 2-hr hydrogen activation at a temperature 10°C higher than the previous operating temperature preceded operating periods.

[d] Approximate.

hydrocarbons on the accessibility of the catalytic surface, possibly according to the following scheme:

The molecular weight of the hydrocarbons *adsorbed on the catalyst* in atmospheric-pressure operation has been found to be greater than that on the catalyst at 7.8 atm. The molecular weight of the synthesis products collected from the middle-pressure synthesis was higher than that of the products obtained at atmospheric pressure. Synthesis at 7.8 atm produced hydrocarbons of higher molecular weight than at atmospheric pressure and probably caused condensation of hydrocarbons present in low concentrations, which would be gaseous at atmospheric pressure, and resulted in a greater fraction of liquid hydrocarbons than at atmospheric pressure. These liquid products flowed over the catalyst and continuously extracted the very high-molecular-weight products which would otherwise have accumulated on the catalyst. However, operation at 7.8 atm probably filled the pores with hydrocarbons, so that the surface was less accessible in subsequent operation at atmospheric pressure, although the rate of diffusion at 7.8 atm may be sufficiently great so that

the hydrocarbon layers do not impede the reaction. This may explain the progressive decrease in activity at 7.8 atm, when the pressure was alternated between 1 and 7.8 atm.

Weller, Hofer, and Anderson [58] observed that cobalt catalysts carburized with carbon monoxide had a low activity in the synthesis at atmospheric pressure. Hydrogenation of the carbide increased the activity considerably, and subsequent carburization again decreased it to a very low value. This cycle could be repeated many times.

X-ray diffraction data (Chapter 2, p 42) showed no detectable amount of bulk-phase carbide in catalysts used in the synthesis; the x-ray patterns were identical with those of the freshly reduced catalyst and showed a pattern of disordered cobalt. Also, the cobalt of the catalyst was not oxidized in the synthesis, which is consistent with thermodynamic data for reduction of cobalt oxide (Chapter 1, Table 16, p 29). Catalysts carburized in carbon monoxide and hydrogenated to remove the carbide gave the diffraction pattern of α-cobalt; a transformation from the disordered cobalt to α-cobalt had occurred in the formation and hydrogenation of the carbide. Because this transformation did not occur in the synthesis and because of the low activity of carburized catalysts, it was concluded that bulk-phase cobalt carbide is neither an intermediate in the synthesis nor a catalyst for it. This conclusion was confirmed by synthesis tests in which Anderson, Hall, Krieg, and Seligman [13] studied the activity and selectivity of a Co-ThO_2-kieselguhr catalyst that was carburized under conditions that formed carbide, carbide plus free carbon, and chiefly free carbon. Surface-area changes in a similar series of carburization experiments are presented in Table 4. The synthesis data summarized in Table 19 showed that carburization (*b*) at 208°C caused decreased activity and increased production of CH_4 and C_1–C_4 hydrocarbons. Hydrogenation at 208°C (*c*) partially restored the activity of the catalyst. In the following carburization and reduction cycles at 208°C (*d–h*), the hydrogenated catalyst was more active and had a more favorable product distribution than the preceding carburized one, but the activity of the catalyst decreased steadily and larger fractions of methane and light hydrocarbons were formed. Thus, carbide formation had a marked effect on both activity and product distribution. Repeated cycles of carburization and reduction at 208°C caused a gradual decrease in activity and a shift toward formation of lighter hydrocarbons that was superimposed on the effect of carbide on activity and product distribution. Carburization at 275°C (*i*) and subsequent reduction at 208°C (*j*) did not significantly change the activity of the catalyst. Finally, reduction at 400°C increased the activity to that of period *c*, but distribu-

[58] S. Weller, L. J. E. Hofer, and R. B. Anderson, *J. Am. Chem. Soc.*, **70**, 799 (1948).

tion of products was less favorable than in period *c*. Thus, "free" carbon did not decrease the activity appreciably but had a marked effect on the product distribution. It has been shown that factors which decrease the accessibility of the catalyst surface usually increase the fraction of lighter hydrocarbons formed.[13, 59] Possibly the increase in the fraction of light hydrocarbons from catalysts containing considerable amounts of free carbon may be related to a decrease in accessibility of the surface. The data of Table 4 indicated that carburization at 275°C poisoned the catalyst with respect to its ability to form carbide. However, the synthesis data in Table 19 indicated that a catalyst poisoned in this manner was quite active in the synthesis.

Table 19. Effect of Carburization and Hydrogenation on Activity and Product Distribution of Cobalt Catalyst 108B [a]

(Space velocity of synthesis gas per hr was 100.)

Period	Pretreatment				Synthesis Conditions			Produets, g per eu m of synthesis gas reacted			
	Gas	SVH	Temperature, °C	Time, hr	Time, hr	Average Temperature, °C	Per Cent of Synthesis Gas Reaeted	CH_4	$C_3 + C_4$	C_1-C_4	Liquids and Solids
a	H_2	3,000	360	2	73	173	66.6	21.8	27.2	55.9	105.7
b	CO	100	208	16	126	195	47.4	41.8	37.8	90.1	64.4
c	H_2	100	208	16	149	190	63.8	27.7	38.7	72.6	106.9
d	CO	100	208	16	149	191	32.7	41.6	33.0	82.3	....
e	H_2	100	208	16	127	190	51.7	34.8	....	.....	81.8
f	CO	100	208	16	176	193	22.9	84.3	....	.....	.....
g	H_2	100	208	16	126	190	42.3	.....	....	.....	.....
h	CO	100	208	16	125	191	17.5	122.9	53.7	189.1	46.9
i	CO	100	274	15	149	191	18.9	106.3	18.5	132.3	10.6
j	H_2	100	208	16	119	191	56.3	73.5	34.5	108.2	15.8
k	H_2	100	200	2	165	189	48.9	83.2	47.2	137.4	18.4
l	H_2	3,000	360	2	166	190	64.5	36.7	45.9	98.6	76.1

[a] R. B. Anderson, W. K. Hall, A. Krieg, and B. Seligman; see reference 13.

Recent work of Prettre and Perrin [39a] indicates that nickel catalysts, pretreated with carbon monoxide to convert an appreciable fraction of the nickel to carbide, had a very low activity in the Fischer-Tropsch synthesis, and hydrogenation of a carbided catalyst increased the activity. Thus, the behavior of cobalt and nickel catalysts is similar in this respect.

[59] R. B. Anderson, A. Krieg, B. Seligman, and W. Tarn, *Ind. Eng. Chem.*, **40**, 2,347 (1948).

Anderson, Hall, Seligman, and Kelly [60] found that the activity of a series of Co-ThO_2-MgO-kieselguhr catalysts was approximately proportional to the total surface area or the area of cobalt metal, as determined by the chemisorption of carbon monoxide (Figures 42 and 43). This

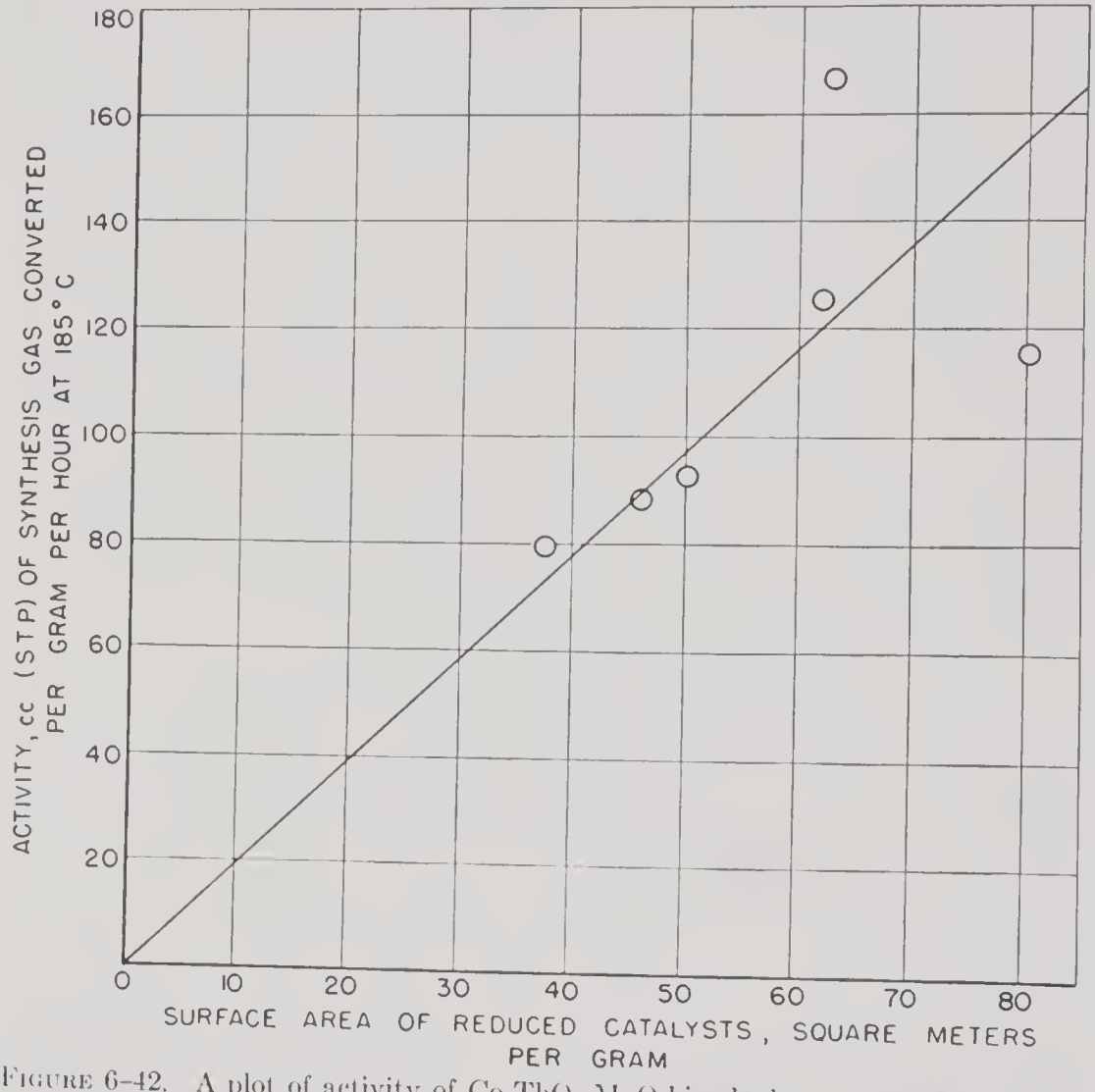


FIGURE 6–42. A plot of activity of Co-ThO_2-MgO-kieselguhr catalysts against the surface area of the reduced catalyst. Activity and area data are given per gram of unreduced catalyst. Reproduced from reference 60.

linear relationship should be expected only if the surfaces of the catalysts are approximately equally accessible.

From the slope of the best line for activities plotted against total surface areas of reduced catalysts, the volume of synthesis gas converted per square meter of surface was found to be only 1.93 cc (STP) per hr at 185°C. The slope of the activity versus chemisorbed carbon monoxide line was 35.6 cc (STP) of synthesis gas converted per cc (STP) of chemi-

[60] R. B. Anderson, W. K. Hall, B. Seligman, and R. Kelly, unpublished results.

sorbed carbon monoxide per hr. Thus, 35.6 molecules of synthesis gas or 11.9 molecules of carbon monoxide per molecule of chemisorbed carbon monoxide were converted per hour, and the average molecule of carbon monoxide remained on the surface for about 5 min before reacting.

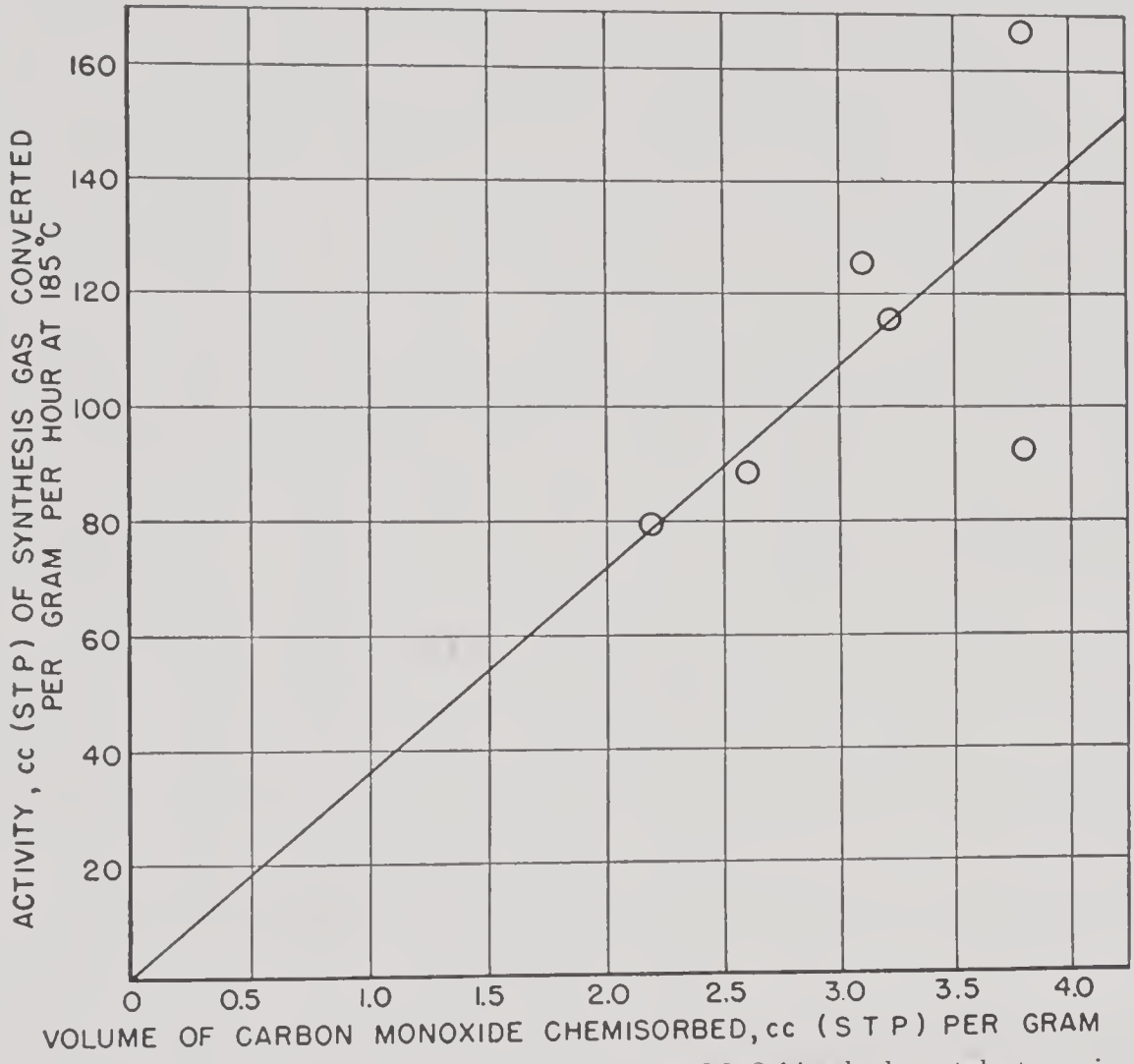


FIGURE 6–43. Correlation of activity of Co-ThO_2-MgO-kieselguhr catalysts against the volume of chemisorbed carbon monoxide at −195°C. Activity and adsorption data are given per gram of unreduced catalyst. Reproduced from reference 60.

These data illustrate in a very striking manner the fact that the Fischer-Tropsch synthesis is an *extremely slow catalytic reaction*. Either only a very minute fraction of the surface is active and accessible or an extremely slow reaction at the catalytic surface is rate controlling.

A Possible Rate Equation for the Synthesis

A satisfactory rate equation for the synthesis on cobalt catalysts must have the following properties: (*a*) The rate increases with total pressure at low pressures but becomes relatively independent of total pressure at

atmospheric pressure and above; (*b*) the rate is relatively independent of partial pressures of components; (*c*) the rate of synthesis is at a maximum for $2H_2 + 1CO$ gas; and (*d*) the rate increases with temperature.

Anderson and Lecky [61] considered the application of the rate equations of Hougen and Watson [62] to the data summarized in Figures 28–31. The high temperature dependence of the synthesis probably excludes diffusion to the catalyst particle as a rate-determining step. Rate equations for adsorption of hydrogen and carbon monoxide as rate-controlling steps are too dependent on partial pressures of these components to fit the observed data. Many of the characteristics of the kinetic data are predicted by an equation in which the rate of desorption of the growing chains from the surface is the rate-controlling step, *ie*, the rate is proportional to the fraction of the surface covered by these groups. An equation of this type for the hydrogenation of ethylene is given in Chapter 2, p 80, equation 27. It is assumed that the equivalent pressure of these growing chains is proportional to a quantity β, where $\beta = p_{H_2}{}^2 p_{CO}$ and that these groups are more strongly adsorbed than other components of the system. The rate equation may then be represented by

$$r = \frac{ab\beta}{1 + b\beta} \tag{2}$$

where a is the product of effective surface area times rate of desorption and b is a term related to the heat of adsorption of the growing chains. Equation 2 may be arranged in the linear form

$$\frac{1}{r} = \frac{1}{a} + \frac{1}{ab\beta} \tag{3}$$

From Figure 28 the slopes of the rate curves, the differential reaction rates, were determined graphically at equal intervals of 1/SVH, and the partial pressures of components at these values of 1/SVH were determined from Figures 29–31. This method of determining rates and partial pressures is not too accurate, and the data have a relative uncertainty of at least ±5 per cent. Plots of equation 3 for data of tests with $2H_2 + 1CO$, $3.5H_2 + 1CO$, and $1H_2$ to $1CO$ gases are shown in Figures 44 and 45. This equation fits the data satisfactorily except that the observed rates in the initial portions of the bed (high values of β) are considerably higher than predicted by the line that best approximates the rest of the data. The values of constants of equation 2 are given in Table 20. Only the values of constants of experiments 8 and 10, and 11 should be

[61] R. B. Anderson and J. Lecky, unpublished work.

[62] O. A. Hougen and K. M. Watson, *Ind. Eng. Chem.*, **35**, 529 (1943).

compared, since the other experiments were made at different periods in the life of the catalyst, when the activity had changed considerably. In Table 20, the values of constant b are large numbers with respect to 1. When about half of the synthesis gas has been converted, values of β vary from 0.03 to 0.04 and $b\beta$ from 6 to 8. In experiments 8, 10, and 11

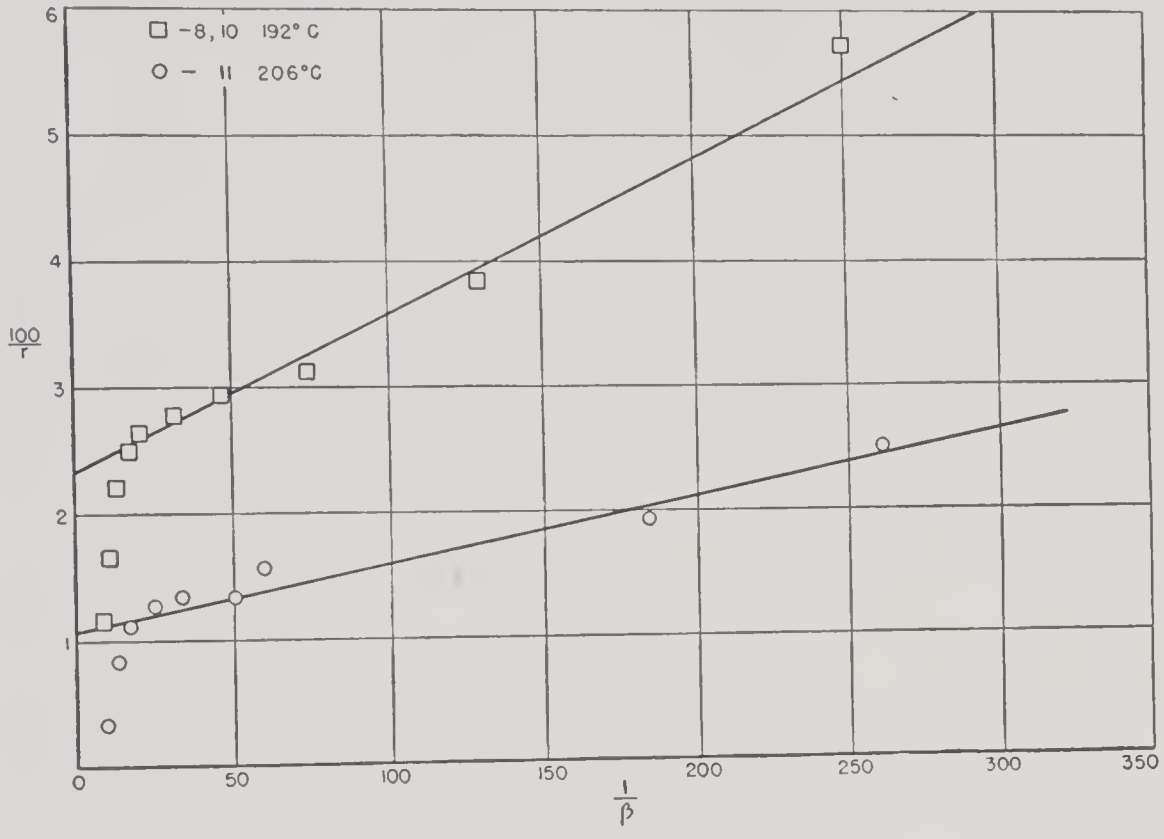


FIGURE 6–44. Plots of equation 3 for data of tests with $2H_2$ to 1CO gas. Reproduced from reference 61.

the activation energy of the rate of desorption term a was 24.5 kcal per mole, which compares well with observed apparent activation energies, while term b was relatively independent of temperature. Equation 2 predicts a maximum synthesis rate with $2H_2 + 1CO$ gas. With $b =$

TABLE 20. VALUES OF CONSTANTS OF RATE EQUATION [a]

Experiment	Gas Composition	Temperature, °C	a [b]	b [c]
8, 10	$2H_2$ to 1CO	192	43.0	187
11	$2H_2$ to 1CO	206	93.0	207
4, 5, 6	$3.5H_2$ to 1CO	186.5	77.0	245
14, 15	$1H_2$ to 1CO	197	18.8	134

[a] R. B. Anderson and J. Lecky; see reference 61.
[b] Cubic centimeters (STP) converted per cc of catalyst per hr.
[c] Atmospheres^{-3}.

200 and $\beta = 0.04$ at atmospheric pressure, the relative rates of synthesis predicted by equation 2 are 0.008, 0.228, 0.50, 0.89, and 0.999 at 0.1, 0.33, 0.5, 1.0, and 10.0 atm, respectively. The equation also predicts that the space-time-yield will increase with space velocity, but the limiting space-time-yield is less by a factor of 1.5–2.0 than that observed.

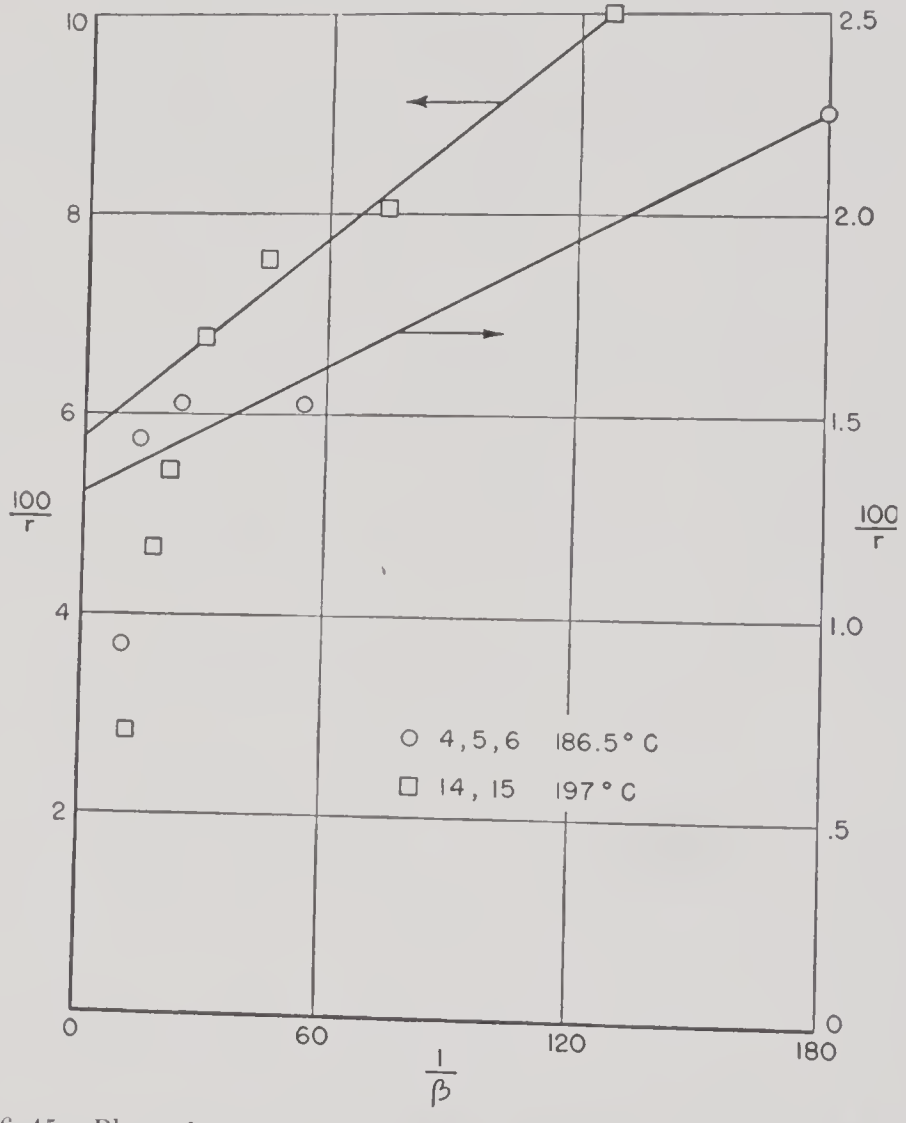


FIGURE 6–45. Plots of equation 3 for data of tests with $3.5H_2$ to 1CO and $1H_2$ to 1CO gas. Reproduced from reference 61.

This is the range where the equation did not satisfactorily fit the data. The lack of agreement of equation 2 at the initial part of the bed (high values of β) may be related to two causes: First, the rate in the initial part of the bed may be sufficiently great to produce higher local temperatures and thus a greater rate of synthesis; or, second, a different process may be rate-controlling in this part of the bed.

It may be concluded that the simple equation for desorption as the rate-determining step approximately fits the experimental data for vari-

ation of gas composition, flow, and possibly total pressure. The variation of the constants of the rate equation with temperature appears reasonable.

IRON CATALYSTS

Kinetics

The synthesis on nickel and cobalt catalysts is similar in many respects, but the synthesis with iron catalysts is quite different. First, iron catalysts produce carbon dioxide as the predominant oxygenated product; second, the rate of reaction is more dependent upon operating pressure; and, third, carbides and oxides of iron are found in sizable amounts in used iron catalysts. Very few kinetic data on the synthesis with iron catalysts have been published, and most of those described in this section are taken from captured German documents or from studies at the U. S. Bureau of Mines. Methods of pretreating iron catalysts vary considerably. Some catalysts are merely reduced in hydrogen, whereas others are pretreated with carbon monoxide or carbon monoxide and hydrogen. These methods of induction have been described in Chapter 3.

The activity of iron catalysts decreases rapidly at atmospheric pressure unless the catalysts are carefully inducted and frequently extracted with solvent. In the middle-pressure range, the activities of some catalysts remain constant for periods of 2 or more months. The optimum operating pressure has been found to be between 10 and 30 atm. Data of Pichler [63] in Table 21 indicate that the initial activity of precipitated catalyst was greatest at 30 atm, but the activity at 30 as well as 60 atm decreased rapidly with time. After 2 days at 1 atm, the pressure was increased to 15 atm, and a contraction of 53 per cent was observed at 235°C. After the ninth day of the test at 5 atm, the pressure was increased to 15 atm and the contraction increased to 53 per cent at 235°C. At 15 atm and 237°C, the contractions were greater than 50 per cent for more than 30 days. Thus, with this type of catalyst, about 15 atm was the optimum pressure. This is also shown by data of Scheuermann [64] in which the activity at 12 atm was greater than at 50 or 200 atm. Data of Pichler [23] in Figure 46 indicate that the rate of synthesis varied linearly with total pressure above 1 atm. Extrapolations of the rate-pressure curves do not pass through the origin, and if this is required, the de-

[63] H. Pichler, T.O.M. Reel 101, Documents PG-21,559-NID and PG-21,574-NID; translated in *U. S. Bur. Mines Spec. Rept.*, by M. Leva, 1–67, 1946, Pittsburgh, Pa.

[64] A. Scheuermann in report of H. Zorn, PB 97,368; *F.I.A.T. Final Rept.* 1,267 (1949).

pendence of rate upon pressure for 0–1 atm must be quite large. The slope of the rate-pressure curves increased with temperature. Seligman [42] found that the rate of synthesis on a reduced synthetic-ammonia catalyst (Fe_3O_4-MgO-K_2O) varied directly with operating pressure, as shown

TABLE 21. INFLUENCE OF OPERATING PRESSURE [a]

[Precipitated and alkalized iron oxide catalyst pretreated at 325°C with carbon monoxide-rich gas at 0.1 atm. Constant flow (STP) of synthesis gas.]

Days	1 atm		5 atm		10 atm		30 atm		60 atm	
	Temperature, °C	Contraction,[b] per cent	Temperature, °C	Contraction,[b] per cent	Temperature, °C	Contraction,[b] per cent	Temperature, °C	Contraction,[b] per cent	Temperature, °C	Contraction,[b] per cent
1	235	0	235	30	233	42	235	53	235	50
2	250	0			234	42	235	56	238	42
3			235	25	235	48	234	37	235	40
6			250	38	238	50				
9			270	37	239	50				
12					237	50				

[a] H. Pichler; see reference 63.

[b] These contractions were computed for exit gas without removal of carbon dioxide. Complete conversion corresponds to 55–60 per cent contractions.

in Figure 47. In these experiments the temperature and conversion were maintained constant and the pressure and flow varied. These rate-pressure lines pass through the origin, and their slope increases with temperature.

Many of the experiments on the influence of gas composition on rate of synthesis are difficult to interpret; however, it appears that the rate increased as the hydrogen content increased up to at least $2H_2$:1CO. Scheuermann [64] found that the volumes of carbon monoxide consumed per volume of catalyst per hour were 119 and 142 for $1H_2$:1CO and $2H_2$:1CO, respectively; in these experiments the total flow, temperature, and pressure were maintained constant. The variation in the rate of synthesis is even greater than the variation in the rate of carbon monoxide consumption, since greater ratios of hydrogen:carbon monoxide are consumed with $2H_2$:1CO than with $1H_2$:1CO gas. Pichler [63] studied the

effect of synthesis gas composition as shown in Figure 48. The temperature which produced maximum yields of liquid and solid hydrocarbons, and these yields, are plotted against the percentages of hydrogen in the synthesis gas (presumably at constant total flow and pressure). The

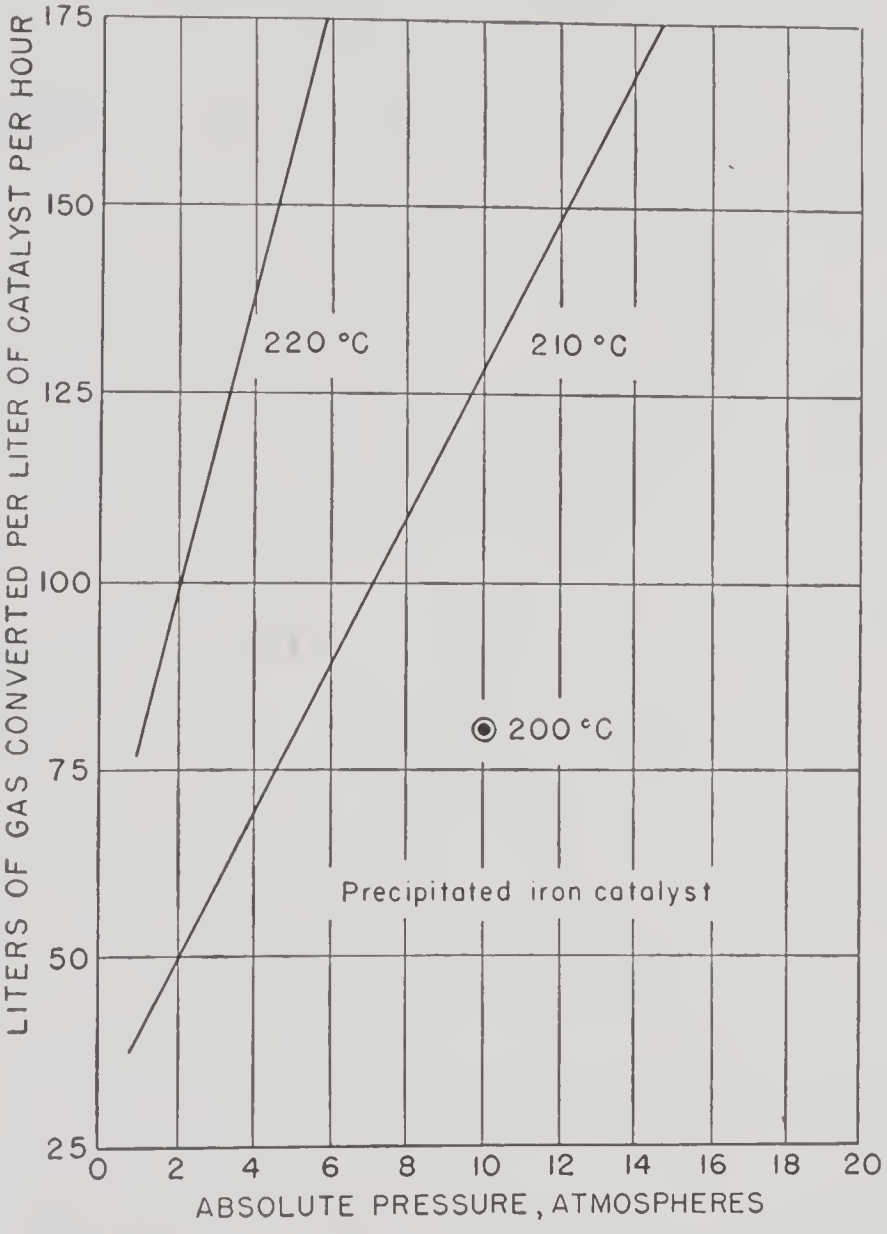


FIGURE 6–46. Variation of space-time-yield in terms of liters of gas consumed with pressure and temperature. Reproduced from reference 23.

yield decreased with increasing hydrogen content of the synthesis gas. Thus, with $1H_2:1.5CO$ gas, the temperature was 235°C and the yield 130 g per cu m; with $4H_2:1CO$ gas, the temperature was 185°C and the yield only 50 g per cu m. Interpretation of these data is not simple, but it appears that the rate of synthesis with $4H_2:1CO$ gas was greater than would have been expected for $1H_2:1.5CO$ gas at the same temperatures.

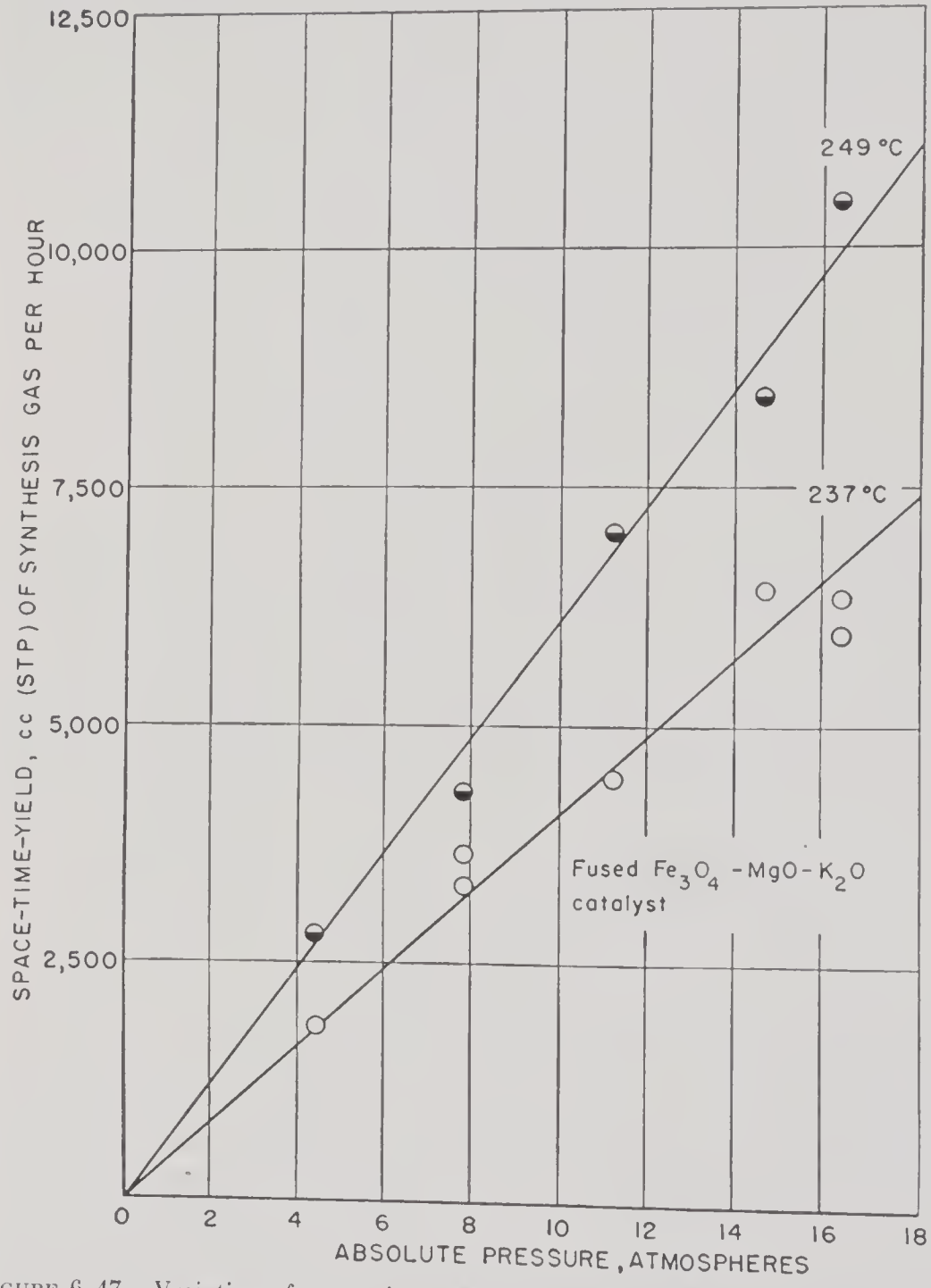


FIGURE 6–47. Variation of space-time-yield at constant extent of conversion with pressure and temperature. From data of reference 42.

Maximum yields per unit volume of synthesis gas may be expected when the gas composition equals the usage ratio. According to Pichler,[63] this occurs at an H_2:CO ratio of 1:1.85 at 15 atm and of 1:2 at 1 atm.

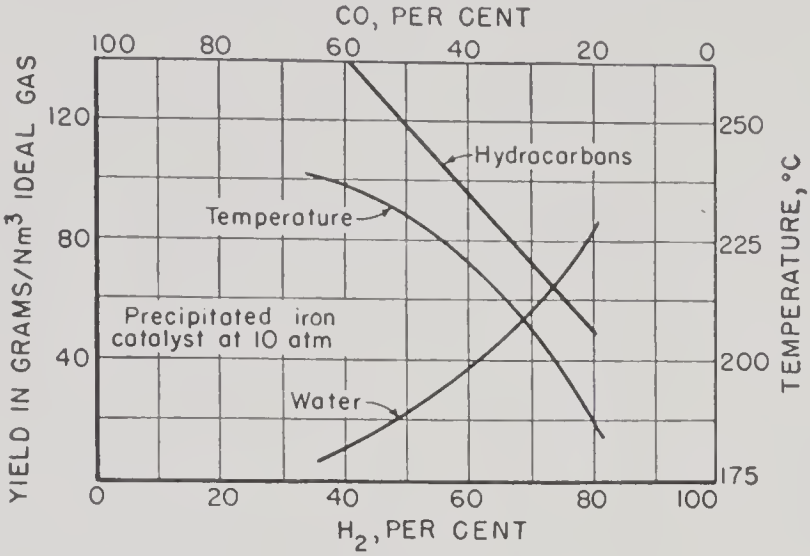


FIGURE 6–48. Variation of the temperature at which maximum yields of liquid and solid hydrocarbons were obtained and the yields of these hydrocarbons and water as a function of gas composition. Reproduced from reference 63.

The H_2:CO usage ratio increased as the ratio of H_2:CO increased, as indicated by the increased production of water in Figures 48 and 49. The usage ratio changed in an interesting manner with space velocity, as shown by data of Seligman and Anderson [42] in Figure 50. In these

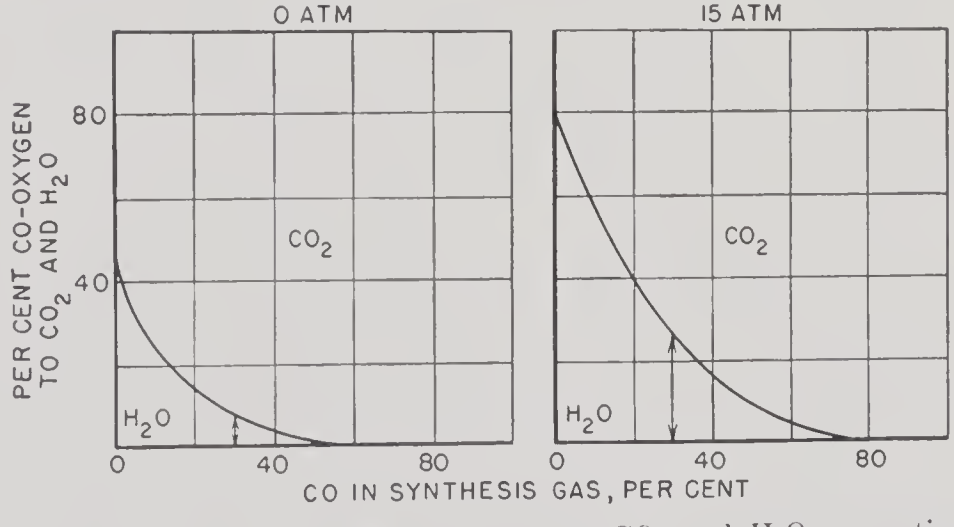


FIGURE 6–49. Conversion of the CO-oxygen to CO_2 and H_2O, respectively, for various synthesis gas compositions at 0 and 15 atm pressure. Reproduced from reference 63.

tests, a fused Fe-MgO-K_2O catalyst was operated with $1H_2$:1CO gas at constant pressure and temperature and the flow was varied. The usage ratio decreased to a minimum and then increased. At low flows at least

90 per cent of the carbon monoxide was consumed, and the ratio of hydrogen:carbon monoxide in the gas at the outlet end of the bed was very high. This may account for the high usage ratios at low flows, which decreased as the flow increased. At flows greater than SVH = 200, the contraction was less than 40 per cent, and the average composition of the gas in contact with the catalyst became more rich in carbon

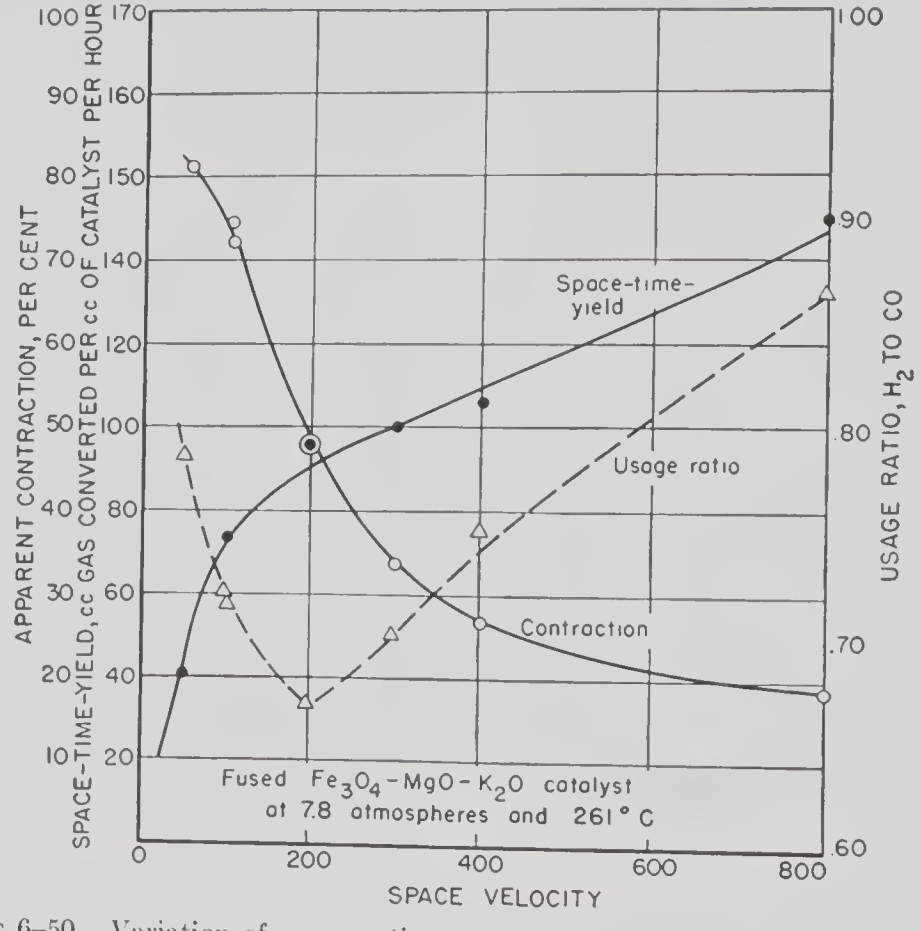


FIGURE 6–50. Variation of usage ratio, gas contraction, and space-time-yield with space velocity. From data of reference 42.

monoxide as the flow was increased, approaching the composition of the feed gas. Thus, the increase in usage ratio cannot be explained by the gas composition. Some workers have suggested that at least part of the carbon dioxide is formed by a secondary water-gas reaction, and the extent of this reaction should be decreased, if the partial pressure of water vapor is decreased by increasing the flow. Thus, the increase in usage ratio with flow in Figure 50 may indicate that at least part of the carbon dioxide is formed by a secondary reaction.

Koelbel and Engelhardt [53] studied the water-gas reaction on a precipitated iron catalyst ($Fe:Cu:K_2CO_3 = 100:0.5:0.25$). Samples of this catalyst were pretreated in four ways: (*a*) carburized in carbon

monoxide for 24 hr at 270°C; (*b*) carburized as in (*a*) and reduced in hydrogen for 24 hr at 270°C; (*c*) reduced in hydrogen for 24 hr at 270°C; (*d*) used in the synthesis with $2H_2:1CO$ gas at atmospheric pressure and 230°C for 24 hr. These catalysts were tested in the water-gas reaction at 240°C and constant flows of $1CO:1H_2O$ gas. After 10 hr testing the following conversions were observed: Catalyst *b*, 80 per cent; *d*, 65 per cent; *a*, 45 per cent; and *c*, 5 per cent. In long periods of testing with $3CO:1H_2O$ gas, the activity of the hydrogenated carbide decreased and the activity of the carbide increased, and after 100 hr both catalysts had the same activity. During this period, the carbidic carbon of the carbide catalyst (*a*) decreased from 6.8 to 4.2 per cent, and the carbidic carbon of the hydrogenated carbide (*b*) increased from 0 to 4.8 per cent. At the same time iron present as iron oxide decreased from 63 to 57 per cent in the carbided catalyst and from 67 to 57 per cent in the hydrogenated carbide. Thus, according to these data, in $3CO:1H_2O$ gas the carbidic carbon content can be either increased or decreased, depending upon its concentration, and iron oxide is reduced.

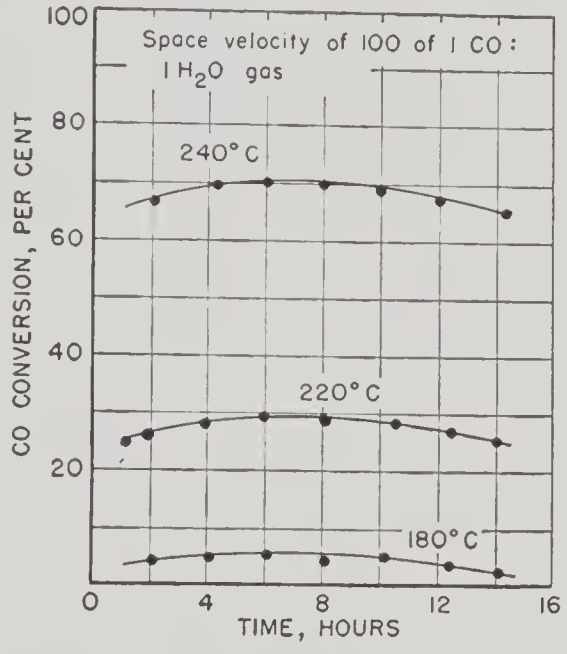


FIGURE 6–51. Conversion of carbon monoxide in a mixture of carbon monoxide and water vapor on a used iron catalyst as a function of temperature. Reproduced by permission from reference 53.

The rate of the water-gas reaction was studied at several temperatures on an iron-copper-potassium carbonate catalyst after use in the Fischer-Tropsch synthesis with $2H_2:1CO$ gas at atmospheric pressure and 230°C for 100 hr. The percentage conversion of the carbon monoxide increased with temperature as shown in Figure 51. These data are similar to those for cobalt catalysts (Figure 35). Thus, if water is the primary product and if it is converted to carbon dioxide by a subsequent water-gas shift reaction, both iron and cobalt catalysts should produce only small amounts of carbon dioxide at 180°C, while at 240°C both catalysts should produce chiefly carbon dioxide. However, in U. S. Bureau of Mines tests of iron catalysts at 7.8 atm of $1H_2:1CO$ gas, no appreciable decrease in carbon dioxide formation with decrease in temperature has been observed in a large number of tests varying in temperature from 215° to 270°C.

Koelbel and Engelhardt [53] studied the usage ratio of H_2:CO in the synthesis on an iron catalyst at atmospheric pressure, in tests in which water vapor was removed by $CaCl_2$ units spaced equally along the length of the catalyst bed. Tests at 230°C (Table 22) indicate that removal of

Table 22. Effect of Water Removal on Usage Ratio of an Iron Catalyst [a]

(Tests with $2H_2$ to 1CO gas at atmospheric pressure.)

Experiment	Conditions	Contraction, per cent	Usage Ratio, H_2:CO	Percentage of Reaction by Way of	
				CO_2	H_2O
1	230°C, SVH = 100 No water removal within catalyst bed	35	0.78	81	19
2	230°C, SVH = 100 Water removal in 4 steps	55	1.25	42	58
3	200°C, SVH = 100 Water removal in 8 steps	25	1.65	18	82

[a] H. Koelbel and F. Engelhardt; see reference 53.

the water vapor increased the usage ratio nearly by a factor of two and also increased the contraction. In test 3 at 200°C a usage ratio of H_2:CO of 1.65 was observed. Thus, in addition to increasing the rate of the water-gas reaction, water vapor appears to decrease the rate of synthesis.

Conversion-reciprocal of space-velocity curves of Scheuermann [64] and Seligman [42] in Figures 52 and 53 have greater curvatures than those observed for cobalt and nickel catalysts, indicating the greater dependence of rate on partial pressures of components in the synthesis.

The rate of synthesis on iron catalysts increases with temperature. In tests with a precipitated iron oxide catalyst in the middle-pressure range, Pichler [63] maintained the contraction constant and varied the gas flow and temperature. When the contraction was kept at 50 per cent (not CO_2-free), the flows were 1.7, 4.1, 8.0, and 16.0 per hr at 220°, 233°, 250°, and 275°C, respectively. In another experiment, contractions of 15 per cent were obtained at 235°C and 280°C at flows of 4 and 20 l per hr, respectively. From these data, overall activation energies of 20 kcal per mole were computed. Similar experiments of Seligman and Anderson,[42] summarized in Figure 54, with a fused and a precipitated iron catalyst with $1H_2$:1CO gas at 7.8 atm also gave activation energies of about 20 kcal per mole. From the pressure dependence data of Figure

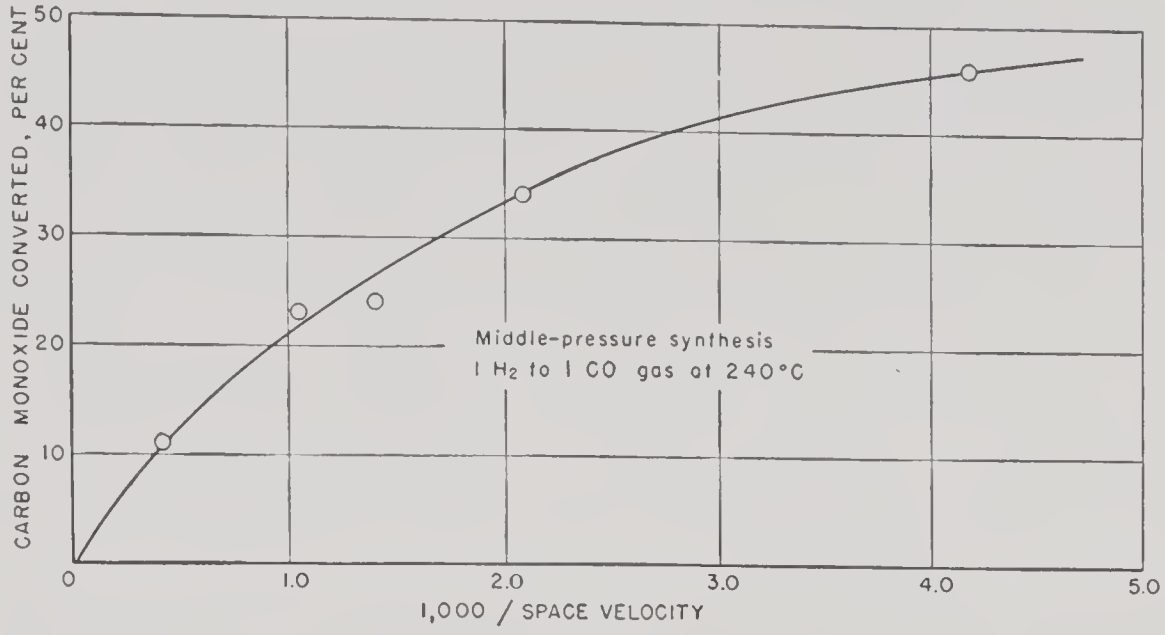


FIGURE 6–52. Variation of the conversion of carbon monoxide with the reciprocal of space velocity with a fused iron catalyst. Reproduced from reference 64.

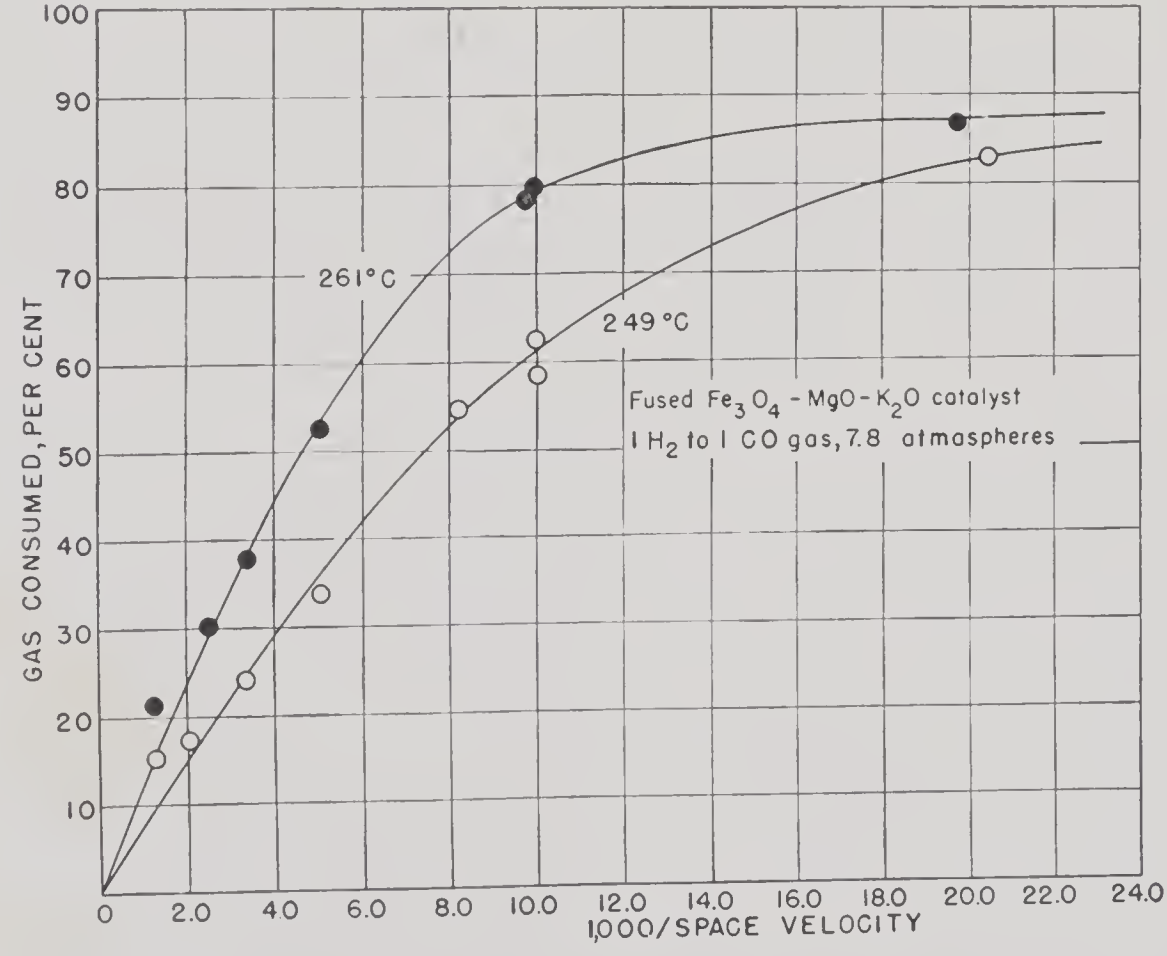


FIGURE 6–53. Variation of conversion with the reciprocal of space velocity. From data of reference 42.

47 activation energies of 18.0 kcal per mole were computed. From data of Schlesinger and Abelson [65] of tests of a fused catalyst in $1H_2:1CO$ gas at 21 atm, activation energies varying from 14 to 17 kcal per mole were computed. Eidus and Altshuller [66] reported an overall activation energy of 28.7 kcal per mole for the synthesis on a precipitated Fe-Cu-ThO_2-K_2CO_3-kieselguhr catalyst at atmospheric pressure.

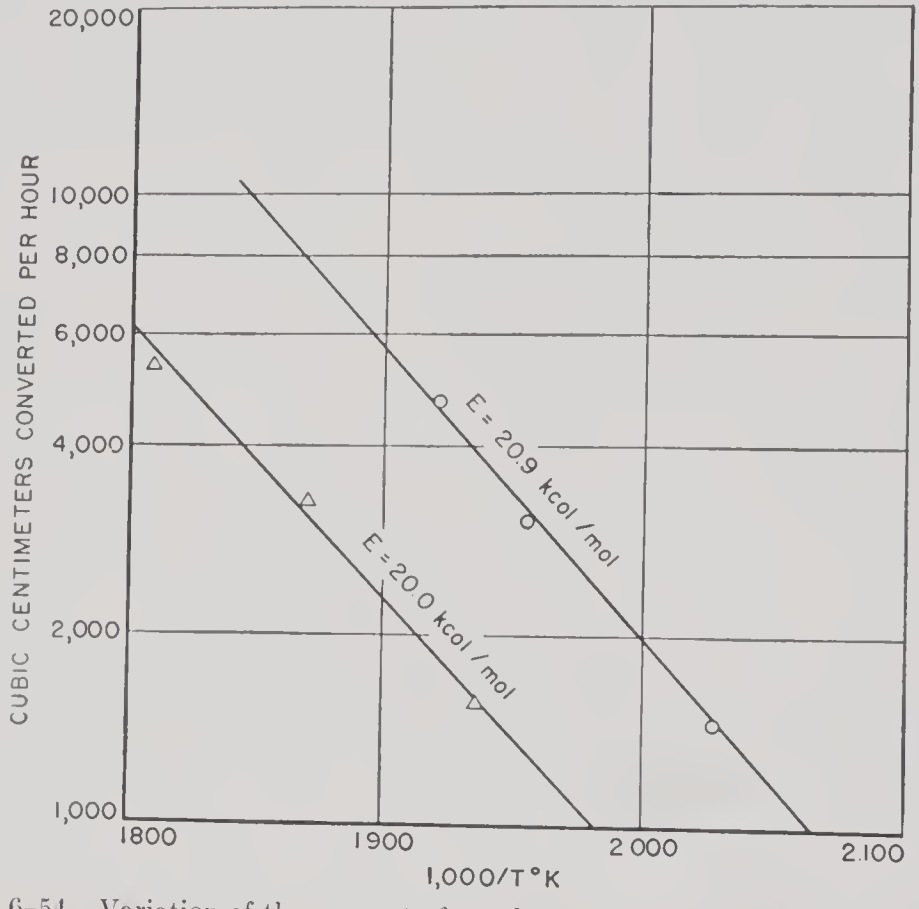


FIGURE 6–54. Variation of the amount of synthesis gas converted per hour with the reciprocal of the absolute temperature, with the apparent contraction held at 65 per cent. ○ represents data for precipitated iron catalyst L2001, and △ represents fused iron catalyst D3001. Reproduced from reference 42.

Data of Shultz, Seligman, and Anderson [67] in Table 80, p 289, of Chapter 3, show that the activity of reduced fused iron catalyst D3001 increased with decreasing particle size, the activity for catalysts varying from 14–18 mesh to 4–6 mesh being approximately proportional to the *external area* of the catalyst. This indicates that only the catalyst in a zone of limited depth from the external surface is effective in the synthesis.

[65] M. D. Schlesinger and M. Abelson, unpublished data.

[66] Y. T. Eidus and S. B. Altshuller, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 349 (1944).

[67] J. F. Shultz, B. Seligman, and R. B. Anderson, *Ind. Eng. Chem.*, to be published.

Physical and Chemical Nature of Used Iron Catalysts

Surface areas of iron catalysts are usually smaller than those of nickel or cobalt catalysts. The areas of reduced fused catalysts containing structural promoters such as alumina or magnesia varied from 5 to 15 sq m per g; the presence of alkali promoters usually did not cause any appreciable change in surface area (Table 2, p 63, Chapter 2). Precipitated iron catalysts usually have gel-like structures with surface areas varying from 100 to 200 sq m per g. However, on pretreatment with synthesis gas or reduction in hydrogen these high areas were decreased to 5–20 sq m per g and the gel structure disappeared. The decrease in surface area presumably occurred when the ferric oxide was reduced, and this sintering was observed on samples of precipitated ferric oxide catalysts reduced only to magnetite. For example, this large decrease in area occurred with $Fe:Cu:K_2CO_3$ (100:10:0.5) catalysts pretreated in synthesis gas at 235°C or reduced in hydrogen at 300°C but did not occur when this catalyst was heated in nitrogen at 400°C.[68]

Used cobalt catalysts usually do not contain carbide or oxide in amounts sufficient to be detected by x-ray diffraction methods, but in used iron catalyst sizable amounts of carbide and oxide, which are detectable by x-ray and thermomagnetic analyses, are usually observed.

Herbst [19] found hexagonal and Hägg Fe_2C in used fused synthetic-ammonia-type catalysts and in precipitated catalysts. Most fused catalysts showed predominantly the x-ray pattern of Hägg carbide, but a few gave chiefly the patterns of hexagonal Fe_2C. Precipitated catalysts, especially those containing copper, gave predominant diffraction patterns of the hexagonal carbide. In a sample of a used synol catalyst containing by analysis 86.6 per cent Fe, 3.42 Al_2O_3, 0.52 K_2O, and 3.6 CaO, but no copper, and presumably operated at low temperatures, principally the hexagonal and a small amount of Hägg carbides were observed. Herbst concluded that the presence of the hexagonal Fe_2C was a necessary but not a sufficient condition for catalysts of high activity.

Pichler and Merkel [20] studied the effect of carbide content of iron catalysts on catalytic activity and the changes in the carbide and oxide content during the synthesis. Their experiments may be divided into two groups: in the first, carbides were determined by acid decomposition, and in the second, by the thermomagnetic method. It appears that their acid decomposition analysis gave low values for carbidic carbon.

In the acid decomposition studies, a precipitated iron oxide gel (presumably alkalized) was pretreated with carbon monoxide at 0.1 atm and 325°C for 24 hr, and the amount of carbidic carbon was determined be-

[68] W. K. Hall, W. Tarn, and R. B. Anderson, *J. Am. Chem. Soc.*, to be published.

fore and after various periods of testing at 235°C and 15 atm. The catalyst activity remained sufficiently high to give fairly complete conversion in all experiments. After 7 days, the carbide content had dropped to about 70–90 per cent of the original amount, and after a total of 112 days the carbide content was still at about this value. In the 112 days, the oxygen content increased from 0.59 to 1.6 g per 100 g of iron. The authors concluded that properly inducted catalysts attained a steady-state composition in the first few days and that the constancy of the activity reflected their constant composition. Catalysts which had become inactive by prolonged operation in the synthesis or operation at high temperature contained considerably less carbidic carbon and more oxide.

In the magnetic studies, a precipitated alkalized iron oxide catalyst containing small amounts of copper was pretreated with carbon monoxide at 0.1 atm and 325°C for 25 hr. This procedure converted the iron to Hägg carbide. Operation in the synthesis at 215°C and 12 atm for 17 days caused no perceptible change in the composition of the catalyst. The difference between this result and those reported in the acid decomposition studies may be due to the lower synthesis temperature in the latter experiment.

A number of catalysts containing copper and alkali were tested in the synthesis at atmospheric pressure without the usual induction in carbon monoxide at 0.1 atm. The catalysts began to form oil after a few minutes of operation. One catalyst was heated in synthesis gas at 225°C until the first exothermic reaction occurred, as indicated by a thermocouple in the catalyst bed. In this brief treatment with synthesis gas, the catalyst was largely converted to magnetite and to a small extent to Hägg carbide. A $Fe:Cu:K_2CO_3$ (100:20:0.25) catalyst was operated at atmospheric pressure and 235°C. After 17 hr the contraction had increased to 14 per cent, and the thermomagnetic curve (Figure 55) showed the presence of Hägg Fe_2C and a large amount of magnetite. After 47.5 hr of operation the contraction was 26.5 per cent, and the magnetic analysis (Figure 56) showed somewhat greater amounts of Hägg carbide. After 121 hr, the catalyst reached its maximum activity. There was only a slight increase in the carbide:magnetite ratio (Figure 57), but the Curie Point at about 390°C indicated the presence of hexagonal carbide in addition to Hägg carbide. The experiments of Pichler and Merkel indicate that the catalytic activity in many cases varies in a direct manner with the amount of Fe_2C present.

Jellinek and Fankuchen [69] reported an x-ray diffraction study of iron

[69] M. H. Jellinek and I. Fankuchen, in *Advances in Catalysis*, vol. I, Academic Press, New York, 1948, p 279.

catalysts presumably used in a fluidized reactor. The catalysts were reduced in hydrogen from magnetite to α-iron before use in the synthesis. After use in the synthesis a sample of one catalyst, which was still highly active, showed only the diffraction pattern of magnetite. A sample of another catalyst that was used for a somewhat longer period and that

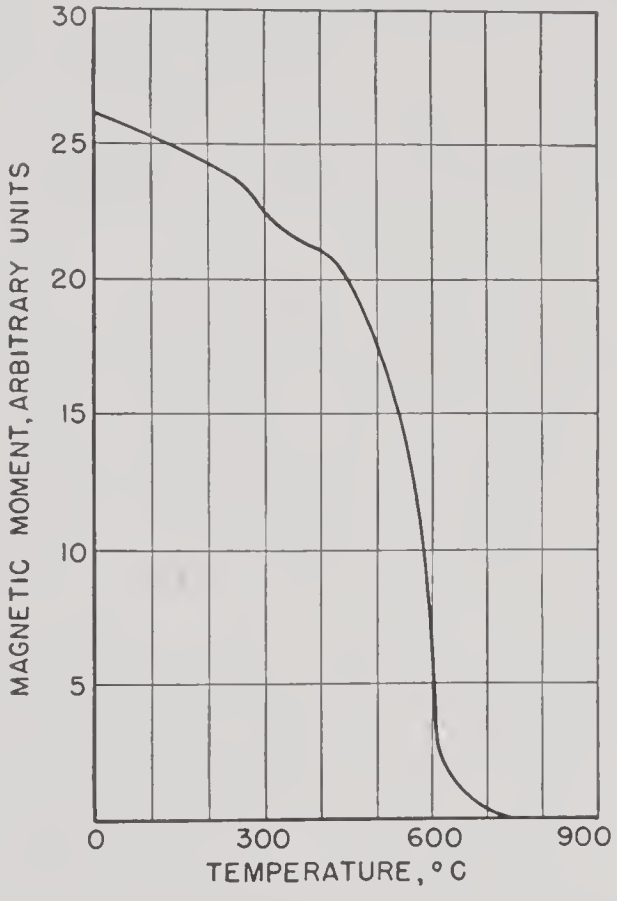


FIGURE 6–55. Thermomagnetic curve of Fe:Cu:K_2CO_3 (100:20:0.25) catalyst, heated in synthesis gas at 1 atm to 235°C and kept at that temperature (time, 17 hr). Reproduced from reference 20.

had a greater activity than the first showed only the diffraction pattern of a carbide, presumably Hägg Fe_2C. These authors were puzzled to find that these two active catalysts had such dissimilar bulk phases.

Hofer, Seligman, Cohn, and Anderson [70] studied the change in composition of reduced fused iron catalyst D3001 (Fe_3O_4-MgO-K_2O) during operation in the synthesis at 7.8 atm of $1H_2$:1CO gas. Portions of the catalyst were removed periodically for thermomagnetic analysis. The position of the Curie points on the thermomagnetic curve indicated that Hägg Fe_2C was the only carbide phase in the used catalysts. The fraction of iron present as Hägg carbide was estimated from the thermo-

[70] L. J. E. Hofer, B. Seligman, E. Cohn, and R. B. Anderson, *J. Am. Chem. Soc.*, to be published.

magnetic curve by extrapolating from a temperature above the Curie Point of Hägg carbide to a lower reference temperature as described in Chapter 2, p 47. Specifically, the magnetic moment of α-iron plus magnetite was determined at 325°C (at which the moment of Hägg carbide is essentially zero); and from the known variation of the moment of these phases with temperature, the magnetic moment of α-iron plus

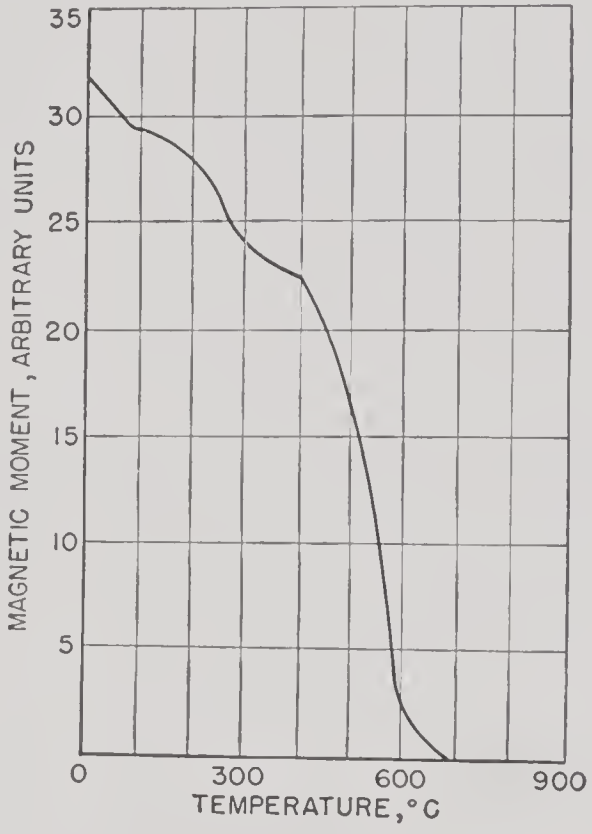


FIGURE 6–56. Thermomagnetic curve of Fe:Cu:K_2CO_3 (100:20:0.25) catalyst, heated to 235°C in synthesis gas at 1 atm and kept at that temperature (time, 47.5 hr). Reproduced from reference 20.

magnetite at room temperature was computed. The difference between the total moment observed at room temperature and the extrapolated value is the moment of Hägg carbide, and the iron as carbide is computed from this difference. From the moment of α-iron plus magnetite and the ratios of these phases from x-ray analyses, the iron as α-iron and magnetite can be computed. Thus, from the magnetic and x-ray data, the weight of iron in ferromagnetic forms was computed. This value was subtracted from the total iron obtained from chemical analysis, and the difference was termed "non-magnetic iron." Presumably, the non-magnetic iron is present in crystallites of normally ferromagnetic phases, which are too small to exhibit ferromagnetism.

In U. S. Bureau of Mines test X194 the catalyst was operated at 234°C

for the first 46 hr. In the next 1,830 hr the temperature was held at about 257°C and the flow of synthesis gas was varied to maintain a constant contraction of 64 per cent (CO_2-free). In this period the activity expressed as space-time-yield was approximately constant. After this period, the temperature was increased in several steps to 300°C to determine the effect of higher temperatures on the phases of catalyst.

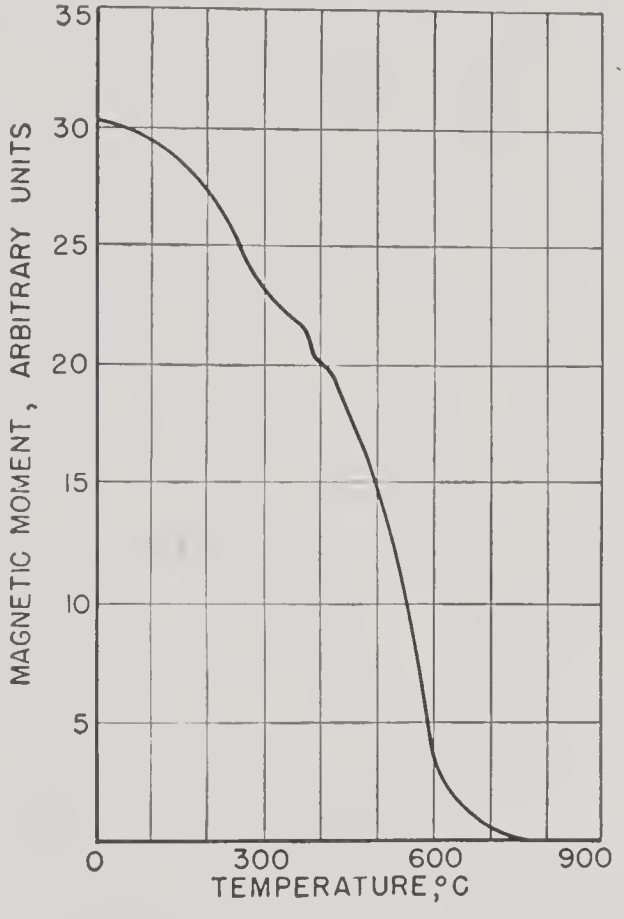


FIGURE 6–57. Thermomagnetic curve of Fe:Cu:K_2CO_3 (100:20:0.25) catalyst, heated to 235°C in synthesis gas at 1 atm and kept at that temperature (time, 121 hr). Reproduced from reference 20.

Figure 58 presents the changes in phases during test X194. The reduced catalyst contained no magnetite, and about 70 per cent iron was present as α-iron and 30 per cent as non-magnetic iron. In the first 46 hr of testing (at 235°C) the iron as Hägg carbide increased to 18 per cent, and the maximum iron as carbide (29 per cent) was observed at 200 hr. In subsequent testing at 257°C, the iron as Hägg carbide decreased gradually to 21 per cent at 1,800 hr. In the first 600 hr, the iron as α-iron decreased to 16 per cent and iron as magnetite increased to 28 per cent. At 1,800 hr the iron as α-iron and magnetite was 8 and 38 per cent, respectively. When the catalyst was tested at 279° and 300°C, the iron as α-iron and Hägg carbide decreased to 7 and 13 per cent,

respectively, while iron as magnetite increased to 47 per cent. The non-magnetic iron remained essentially constant (30–33 per cent) throughout the experiment.

In another experiment (X168) with the same catalyst (D3001) with $1H_2$ to 1CO gas at 7.8 atm, the space velocity and conversion were maintained constant and the temperature varied. In the first 800 hrs

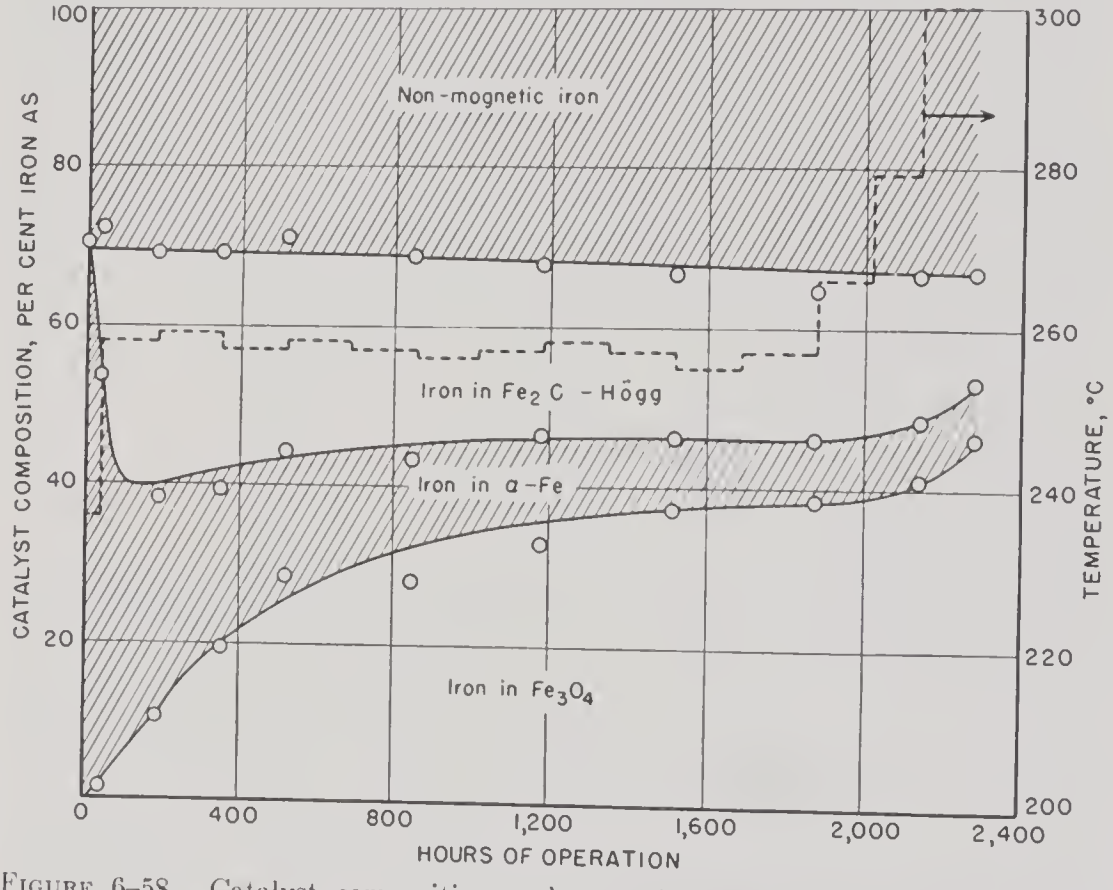


FIGURE 6–58. Catalyst composition and operating temperature changes during experiment X194. From data of reference 70.

the activity decreased continually so that the temperature had to be increased from 250° to 280°C. At this point disintegration of the catalyst particles presumably caused by carbon deposition was observed. At the same time, the activity increased, apparently because of the smaller particle size of the disintegrating catalyst, so that the temperature progressively decreased to 246°C. In the first 67 hr (Figure 59) the iron as Hägg carbide increased to 18 per cent and then steadily decreased to about 8 per cent at the end of the experiment. The non-magnetic iron was 30 per cent in the reduced catalyst and varied from 25 to 22 per cent during the synthesis. Chiefly at the expense of the α-iron phase, the iron as oxide increased rapidly initially to 56 per cent at 800 hr and to 66 per cent at the end of the experiment.

These experiments show that the α-iron of the reduced catalyst was converted to the maximum amounts of Hägg carbide in the first few days of the synthesis. Hexagonal Fe_2C or cementite was not observed in any of the samples. The formation of magnetite was more rapid at higher temperatures so that at 800 hr at temperatures up to 280°C the iron as

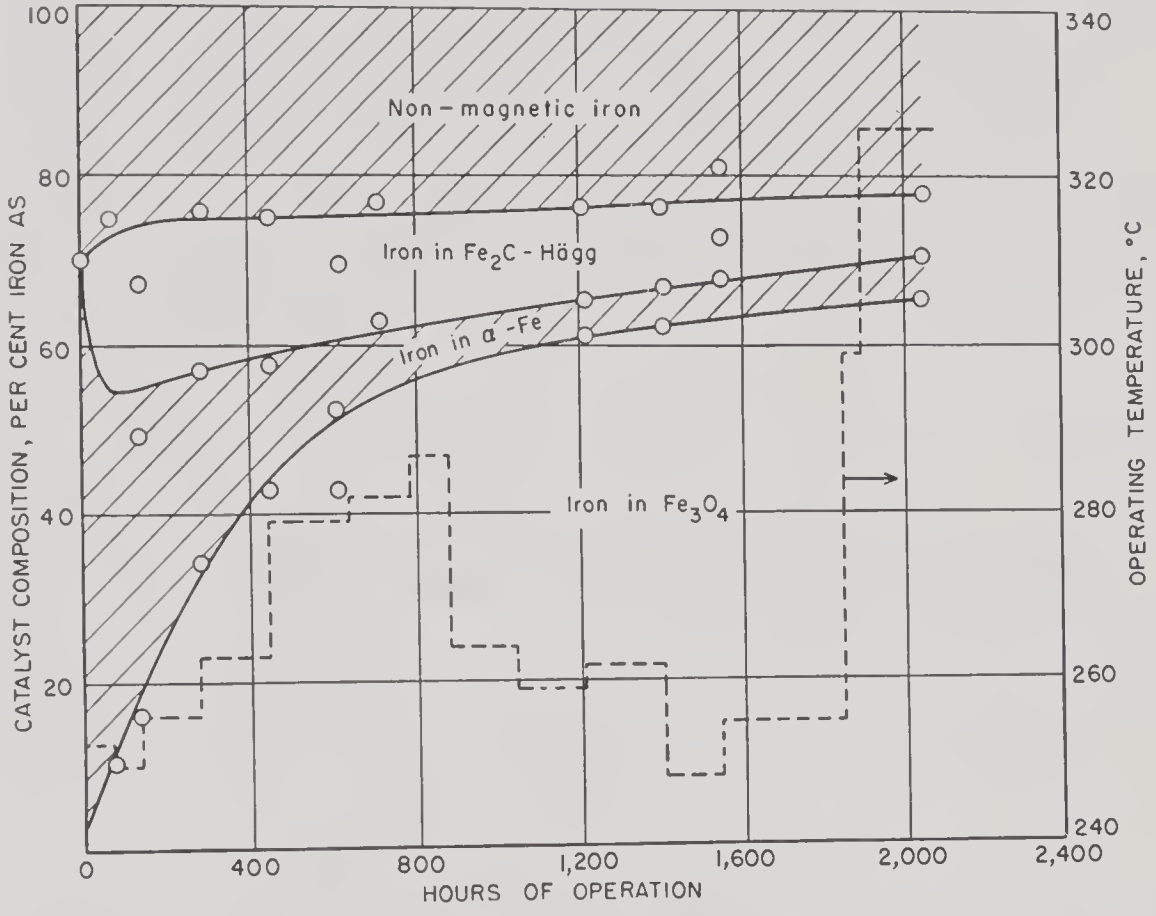


FIGURE 6–59. Catalyst composition and operating temperature changes during experiment X168. Unpublished data.

magnetite was 56 per cent (Figure 59) compared to 33 per cent at 257°C (Figure 58).

Magnetite was formed chiefly from the α-iron phase. The carbide phase decreased more slowly than α-iron phase, and it may be tentatively concluded that carbide phases are more resistant to oxidation than α-iron.

Catalytic activity cannot be simply related to catalyst composition, and possibly the phases found in the catalyst are merely functions of the operating temperature of the synthesis. It is also possible that the active components may be a part of the non-magnetic iron phase, since, small, incomplete, or disordered crystallites may be expected to have the greatest activity. However, in Figure 58 the content of Hägg carbide remained essentially constant over the period of constant activity, as compared with rather large changes in the fractions of α-iron and

magnetite, and in Figure 59 the decrease in activity during the first 800 hr was paralleled by a decrease in the amount of Hägg carbide. The increase in activity after 800 hr in this test is probably influenced more by particle size than by catalyst composition.

German work [71] as well as experiments of the U. S. Bureau of Mines [72] indicated that reduced fused catalysts pretreated so that they contained a large fraction of cementite are more active in the synthesis than reduced catalysts. Pretreated catalysts containing other interstitial phases than the Fe_2C carbides or cementite were more active than reduced catalysts, as shown below for nitrides of iron.

Anderson, Shultz, Seligman, Hall, and Storch [73] showed that nitrides of iron have unique properties as Fischer-Tropsch catalysts. Homogeneous phases in the system iron-nitrogen are: [18]

Phase	Weight Per Cent Nitrogen	Atom Ratio, N:Fe	Arrangement of Iron Atoms
α	<0.2	<0.008	Body-centered cubic
γ'	5.7–6.1	0.241–0.259	Face-centered cubic
ϵ	7.3–11.1	0.314–0.498	Close-packed hexagonal
ζ	11.1–11.3	0.498–0.508	Orthorhombic

The activities of nitrided catalysts were greater than those of corresponding reduced catalysts, as shown by the results of tests of a synthetic-ammonia catalyst (Fe_3O_4-MgO-K_2O) with $1H_2:1CO$ gas at 100 and 300 psig (Figures 60 and 61). In these tests, the flow of synthesis gas and the conversion were maintained constant and the temperature was varied. Thus, the temperature of operation varied in an inverse manner with activity. Tests of reduced catalysts at 100 psig were characterized by increasing temperatures of operation (Figure 60, test X152), and these tests were usually terminated in less than 8 weeks of operation by plugging of the catalyst bed by carbon deposition or related processes. A reduced, nitrided catalyst containing an atom ratio of N:Fe of only 0.032 (α-Fe + γ'-Fe_4N) in test X207A was operated at 240°C; this temperature was lower than that used for the reduced catalysts. After 6 weeks of testing, the catalyst was treated with ammonia under conditions that would convert a reduced catalyst to an N:Fe ratio > 0.45. This treatment lowered the operating temperature to about 220°C (207B). After 8 additional weeks of synthesis this catalyst was reduced

[71] E. H. Reichl, U. S. Naval Technical Mission in Europe, *Rept.* 248-45 (1945), 128 pp; PB 22,841.

[72] J. F. Shultz, B. Seligman, and R. B. Anderson, unpublished data.

[73] R. B. Anderson, J. F. Shultz, B. Seligman, W. K. Hall, and H. H. Storch, *J. Am Chem. Soc.*, **72**, 3205 (1950).

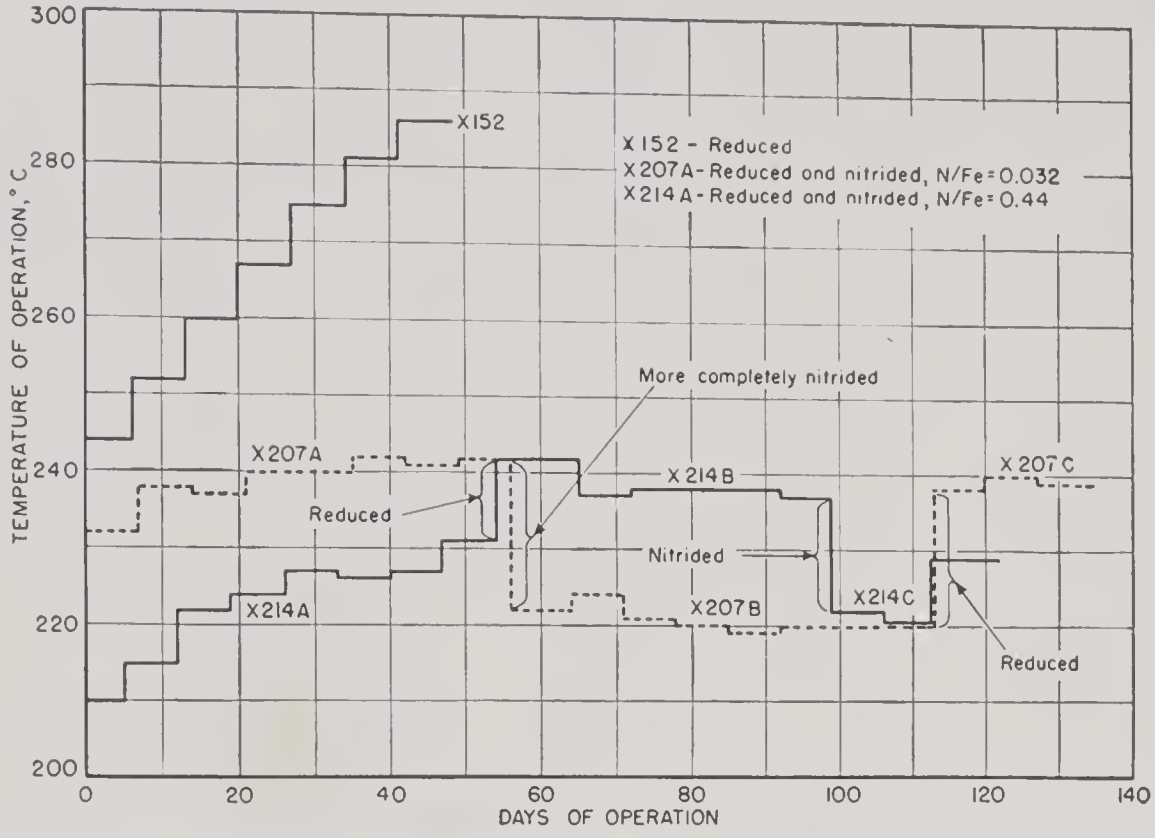


FIGURE 6–60. Temperatures of operation required to maintain constant conversions on reduced and nitrided samples of catalyst D3001 at 100 psig. Reproduced by permission from reference 73.

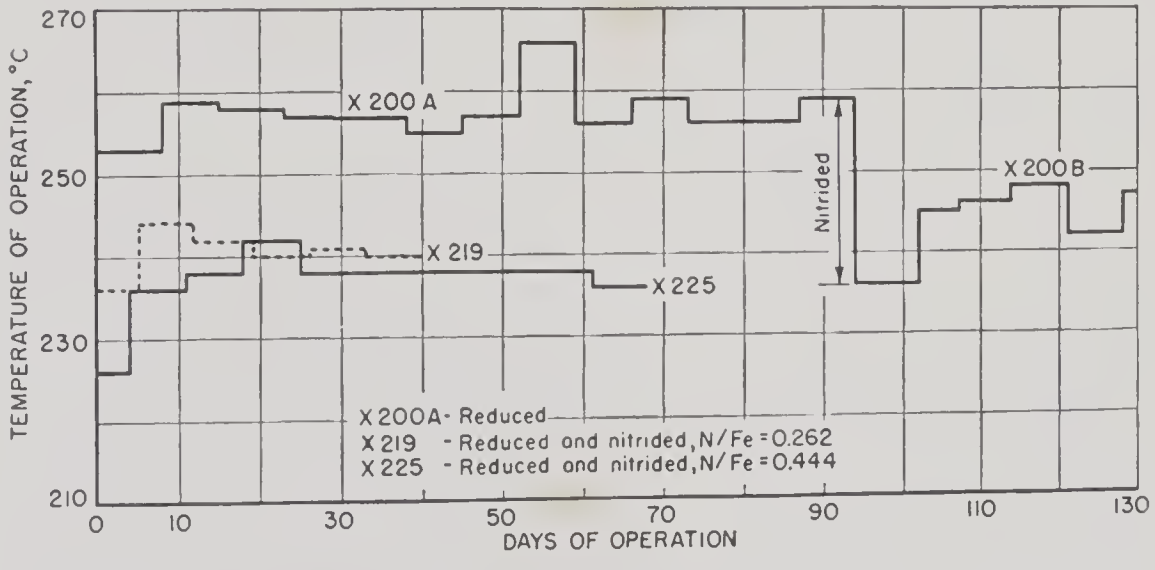


FIGURE 6–61. Temperatures of operation required to maintain constant conversions on samples of reduced and nitrided catalyst D3001 at 300 psig. Reproduced by permission from reference 73.

in hydrogen at 385°C under conditions that should remove all the nitrogen; subsequently, the synthesis temperature had to be increased to 240°C (207C). In test X214A, the catalyst was nitrided to the ϵ-phase (N:Fe = 0.44). In a period of 8 weeks the temperature was increased from 210° to 230°C. At the beginning of the ninth week the catalyst was hydrogenated at 385°C, and the temperature of operation had subsequently to be increased to 239°C (X214B). After the fourteenth week of operation the catalyst was renitrided, presumably to the ϵ-phase, and the temperature of operation was decreased to 225°C.

Tests of reduced synthetic-ammonia catalyst at 300 psig were characterized by nearly constant temperatures of operation, as shown by test X200A in Figure 61. After 13 weeks of testing the catalyst was nitrided, presumably to the ϵ-phase, and the temperature could be decreased to 243°C. Tests of catalysts nitrided to a mixture of γ'- and ϵ-phases (N:Fe = 0.262) in test X219 and to the ϵ-phase (N:Fe = 0.444) in X225 operated at 240°C. Thus, the activities of the nitrided catalysts at both 100 and 300 psig were greater than those of reduced catalysts, but the increase in activity was larger at 100 psig.

The product distribution from nitrided catalysts was considerably different from that of reduced catalysts, as shown in Table 23. In every case, the products from nitrided catalysts were of lower average molecular weight and contained a higher fraction of gaseous hydrocarbons. Nitrided catalysts also produced greater yields of oxygenated compounds, especially alcohols, than corresponding reduced catalysts.

Nitrided catalysts have a greater mechanical stability and longer life than reduced catalysts, presumably because the production of free carbon and iron oxide is very much slower than on reduced catalysts. Tests of reduced catalysts at 100 psig are usually terminated by plugging of the catalyst bed in about 8 weeks of testing; however, after 6 months of testing, a nitrided catalyst in test X215 dropped freely from the reactor and appeared to be the same as when charged into the reactor. Thus, nitriding is a method of preventing mechanical difficulties due to catalyst instability. The nitrogen is only slowly displaced from the nitride, the nitrogen being replaced by carbon to form carbonitrides, as shown in Figure 62 in a test with $1H_2$:1CO gas at 218°C and 100 psig. The total carbon plus nitrogen:iron atom ratio increased in the first week to about 0.50 and did not exceed 0.508 until after 7 weeks. The ratio of carbon plus nitrogen:iron atoms greater than 0.508 must be attributed to free-carbon formation, unless the upper limit of ζ-phase is greater than reported by Jack.[18] X-ray diffraction studies of these catalysts showed that the initial ϵ-phase nitride was converted to ϵ-phase carbonitride. Lines corresponding to oxides of iron were usually not found.

TABLE 23. COMPARISON OF TESTS OF NITRIDED AND REDUCED CATALYST D3001 (Fe_3O_4-MgO-K_2O) WITH $1H_2$:1CO GAS [a]

Pressure, psig	100				300			
Test, X . . .	152	214A	214B	214C	200A	200B	219	225
Reduction in hydrogen								
Temperature, °C	450	450	385	. . .	450	. . .	550	550
Time, hr	43	40	4	. . .	40	. . .	20	20
Space velocity	2,500	2,500	5,000	. . .	2,500	. . .	2,500	2,500
Per cent reduction	91.8	100.8	. . . . .	. . .	92.6	. . .	99.0	98.1
Nitriding in ammonia								
Temperature, °C	. . . .	385	. . . . .	385	. . . . .	385	385	350
Time, hr	. . . .	4	. . . . .	4	. . . . .	4	4	6
Space velocity	. . . .	5,000	. . . . .	1,000	. . . . .	5,000	5,000	1,000
Atom ratio, N:Fe	0	0.44	?	?	0	?	0.262	0.444
Phases present	α-Fe	ϵ-phase	α-Fe + Fe_3C	?	α-Fe	?	α- + ϵ-phases	ϵ- + ζ(?)-phases
Test data								
Weeks averaged	2–5	2–8	10–15	16–18	2–8	13–18	2–5	3–10
Space velocity	98	98	101	99	306	295	296	293
Temperature, °C	263	225	238	224	257	243	242	238
Contraction, per cent	65.0	64.1	63.6	62.6	65.5	63.0	64.0	65.2
Usage ratio, H_2:CO	0.72	0.75	0.75	0.79	0.72	0.80	0.77	0.79
Product distribution, weight per cent of total of gaseous and liquid + solid hydrocarbons (including oxygenated material in oil phase)								
C_1	17.8	20.9	11.9	26.8	12.3	16.6	17.6	16.2
C_2	9.6	10.1	9.0	6.5	7.9	11.7	11.2	9.7
C_3	13.8	15.4	12.8	17.6	9.5	15.3	14.2	11.5
C_4	6.1	9.2	8.3	11.3	6.1	5.6	5.6	6.6
C_1–C_4	47.3	55.6	42.0	62.2	35.8	49.2	48.6	44.0
Liquids + solid [b]	52.7	44.4	58.0	37.8	64.2	50.8	51.4	56.0
Distillation of liquids + solids								
<185°C	38.1	64.0	39.7	56.5	37.6	64.3	57.4	67.3
185°–352°C	35.5	32.0	31.3	32.9	27.9	24.6	31.7	25.0
352°–464°C	14.9	3.3	11.8	10.6	11.9	5.8	6.8	5.2
>464°C	11.5	0.7	17.2	0.0	18.9	4.2	4.1	2.5

[a] R. B. Anderson, J. F. Shultz, B. Seligman, W. K. Hall, and H. H. Storch; see reference 73.

[b] Liquid + solid hydrocarbons include oxygenated compounds dissolved in the hydrocarbon phases.

McCartney and Anderson [74] determined electron diffraction patterns of carburized and used iron Fischer-Tropsch catalysts. Catalysts carburized in carbon monoxide gave electron diffraction patterns corresponding to the same Fe_2C carbides found by x-ray analysis. Used iron catalysts gave only electron diffraction patterns of the adsorbed wax. After careful extraction of the catalyst in toluene, the electron diffraction pattern of magnetite was found (see Figure 1, Chapter 2, p 45). The

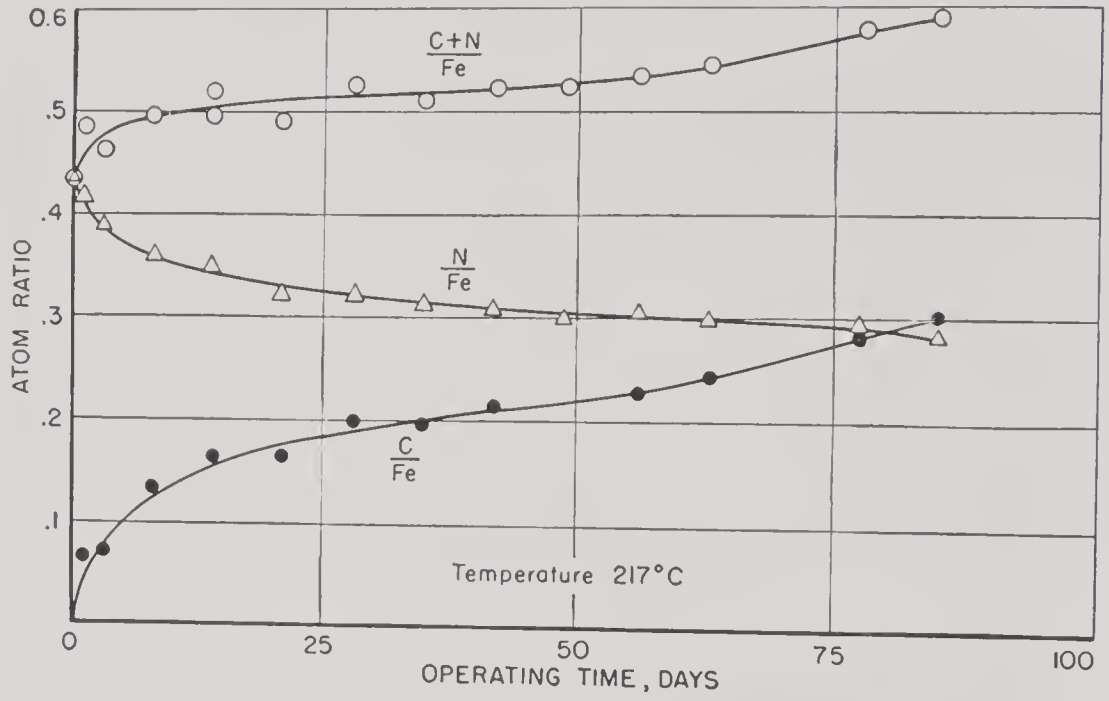


FIGURE 6–62. Nitrogen and carbon content transition of nitrided catalyst D3001 (test X218). Unpublished data.

lines of α-iron and the Fe_2C carbides were not found in any of the electron diffraction patterns of extracted used catalysts, even though in most cases lines of these phases were found in the x-ray diffraction patterns. Thus it appears that the surface of the catalyst was chiefly magnetite, which is consistent with the thermodynamics of formation of magnetite (p 29, Chapter 1). Work of Almquist and Black [75] and Emmett and Brunauer [76] has shown that the surface atoms of iron catalysts were oxidized at ratios of partial pressures of water:hydrogen that were about 0.1 per cent of those required to form bulk-phase oxide. Thus, the formation of both bulk-phase and surface oxides of iron is thermodynamically possible.

[74] T. J. McCartney and R. B. Anderson, *J. Chem. Phys.*, to be published.
[75] J. A. Almquist and C. A. Black, *J. Am. Chem. Soc.*, **48**, 2,814 (1926).
[76] P. H. Emmett and S. Brunauer, *ibid.*, **52**, 2,682 (1930).

Rate Equations for the Synthesis

Only a few studies of kinetics of the Fischer-Tropsch synthesis on iron catalysts are available, and two equations which fit the limited available data for the synthesis on fused catalysts will be considered.

Elliott [77] has shown that the empirical equation

$$\frac{kP}{S} = -\ln(1 - x) \tag{4}$$

where x is the fraction of synthesis gas consumed (the real contraction), P the operating pressure, S the space velocity, and k a rate constant of

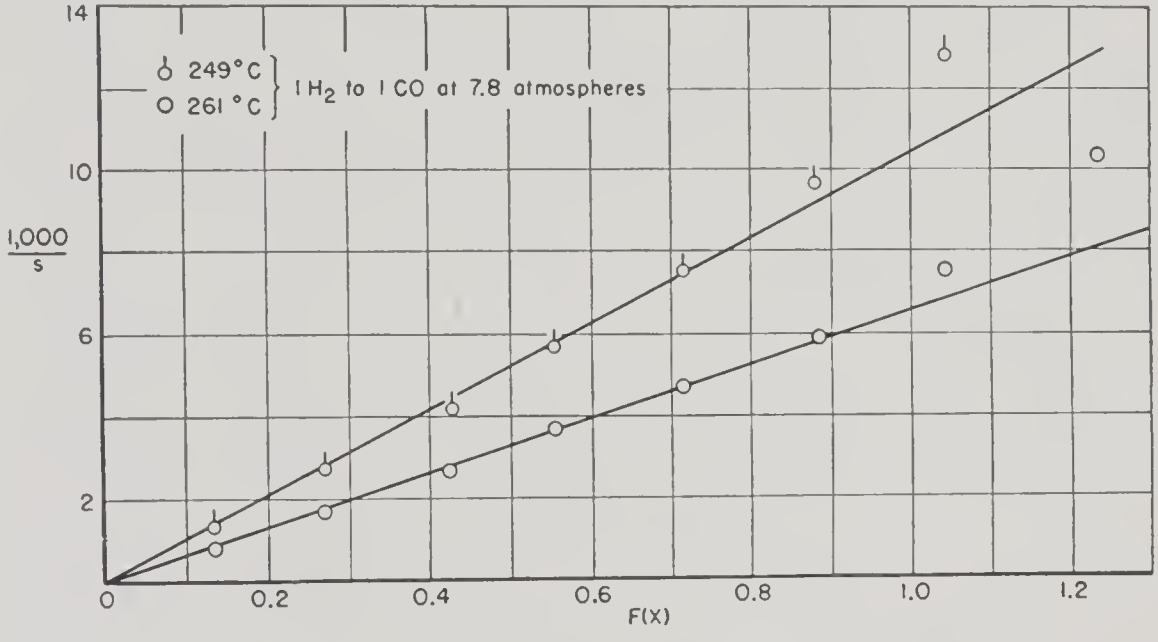


Figure 6–63. A plot of equation 6 for data of fused iron catalyst, D3001. Unpublished data.

the type $k = Ae^{-E/RT}$, in which A is a constant and E the activation energy, fits the data of Figures 47, 52, 53, and 54 quite satisfactorily for tests with $1H_2$:1CO gas. This equation is useful in correlating experimental data.

Seligman and Anderson [42] developed a somewhat similar equation from the assumption that the rate, r, is proportional to the partial pressure of hydrogen, p_{H_2}. Thus,

$$r = \frac{dx}{d(1/S)} = kp_{H_2} = kPN_{H_2} \tag{5}$$

where x is the fraction of $H_2 + CO$ converted, P is the total pressure,

[77] M. A. Elliott, unpublished work.

and N_{H_2} is the mole fraction of hydrogen when the conversion is equal to x. It is assumed that a reaction consuming 3 moles of $H_2 + CO$ produces 1 mole of $H_2O + CO_2$ and that the number of moles of hydrocarbons in the gas phase comprises 7 per cent of the moles of $H_2O + CO_2$. Then the mole fraction of hydrogen is evaluated in terms of x, and equation 5 can be integrated to the following:

$$\frac{kP}{S} = \frac{j}{f}\left\{x + \left(\frac{1}{j} - \frac{1}{b}\right)\ln\left(\frac{1}{1 - bx}\right)\right\} = \frac{j}{f}F(x) \qquad (6)$$

where j has a value of 0.65; $f = U/(1 + U)$, where U is the H_2:CO usage ratio; and $b = f/g$, where g is the fraction of H_2 in the synthesis gas. For $1H_2$:1CO gas and an average usage ratio of 0.75, $f = 0.43$ and $b = 0.86$. This equation approximtaely fits the data of Figures 47, 52, 53, and 54 and predicts that the rate should increase with hydrogen:carbon monoxide ratio as observed by Scheuermann.[64] Figure 63 presents a plot of the reciprocal of space velocity against $F(x)$ (from equation 6) for data of Figure 53. This equation fits the synthesis data in the region from $x = 0$ to $x = 0.6$.

KINETICS OF THE FISCHER-TROPSCH SYNTHESIS WITH RUTHENIUM CATALYSTS

Hydrogen and carbon monoxide are used in the ratio of about $2H_2$:1CO on ruthenium catalysts.[78] At atmospheric pressure the hydrocarbon product was almost exclusively methane. The yields of higher hydrocarbons increased with operating pressure so that at very high pressures solid hydrocarbons predominated.

The rate of synthesis increased with operating pressure to the highest pressure studied, as shown in Figure 64. The slope of the conversion-bed length curve of Figure 65 decreased continuously with increase of bed length, the decrease in slope being greater than observed with iron, cobalt, or nickel catalysts. This implies that the reaction has a large dependence upon partial pressure of components as well as total pressure.

Distribution of Products from the Fischer-Tropsch Synthesis

In addition to explaining the kinetics of the reaction, the correct mechanism for a catalytic reaction should predict the distribution of products. Kinetic data can, at best, reveal only the mechanism of the slowest of a series of reaction steps. Thus, detailed data of the product

[78] H. Pichler and H. Buffleb, *Brennstoff-Chem.*, **21**, 257, 273, 285 (1940).

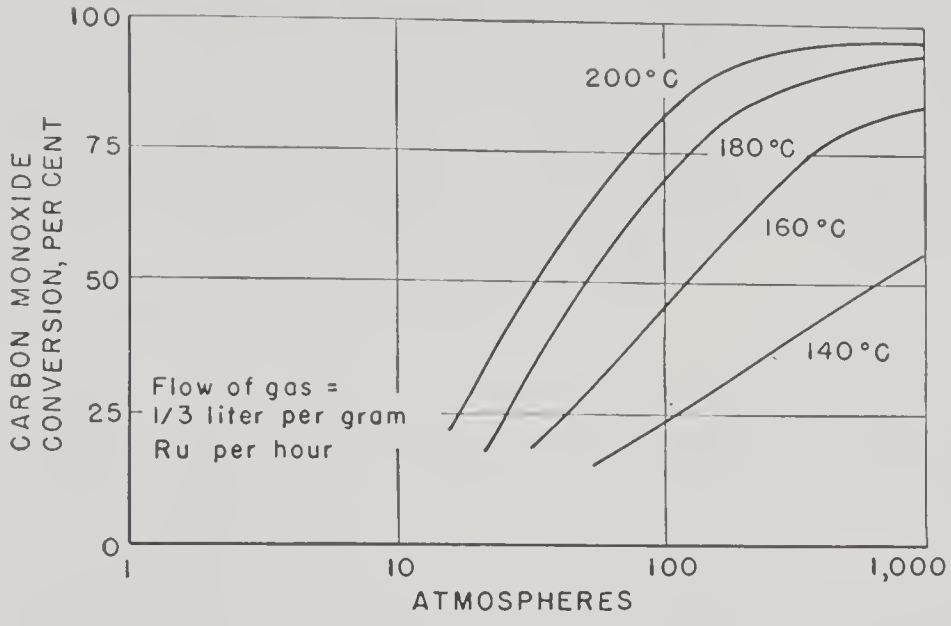


FIGURE 6–64. Variation of the extent of conversion with pressure on ruthenium catalysts. Reproduced from reference 78.

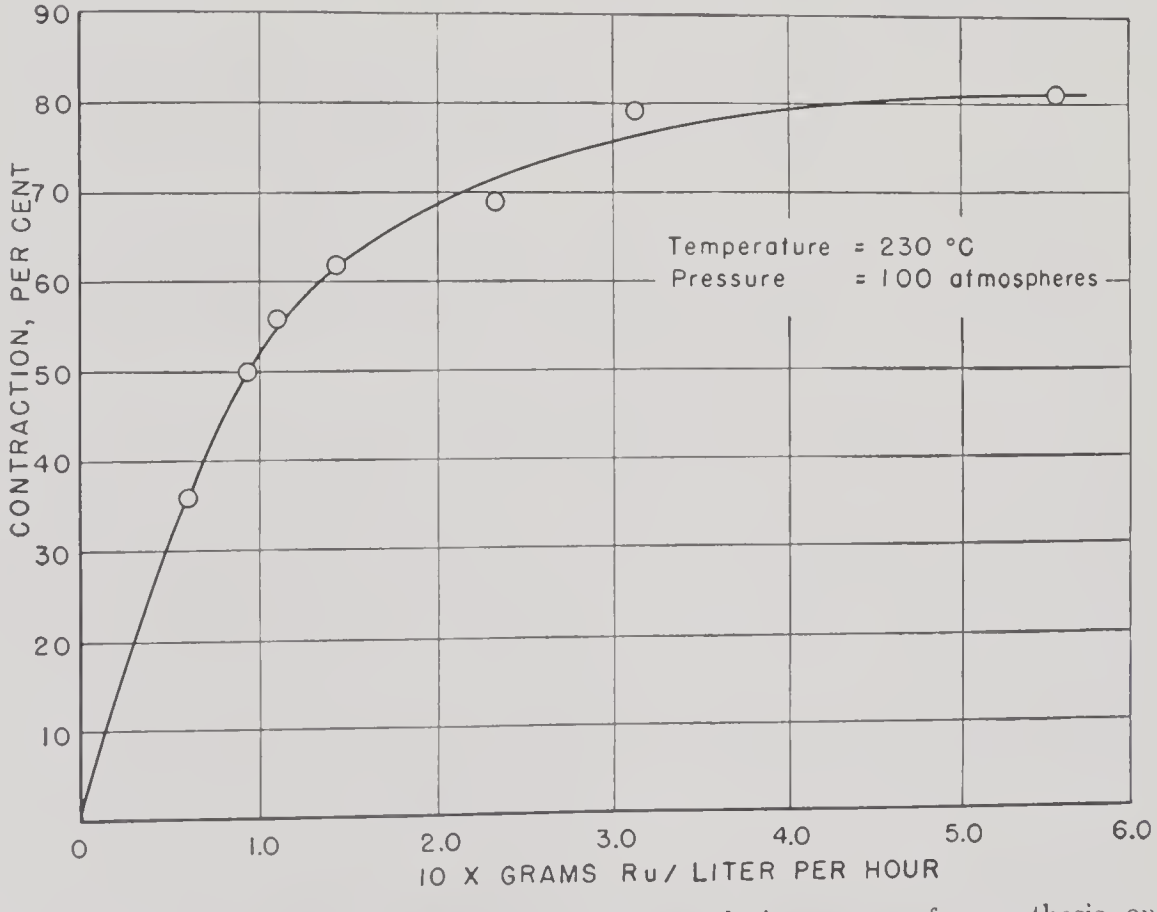


FIGURE 6–65. Conversion-reciprocal of space-velocity curves for synthesis on ruthenium catalysts. Reproduced from reference 78.

distribution and its dependence on operational variables are necessary for the discussion of reaction mechanisms to be presented in the last section of this chapter.

OXYGENATED COMPOUNDS

The formation of water and carbon dioxide has been discussed in the previous section. With nickel, cobalt, and ruthenium catalysts, water is the chief oxygenated product; most of the carbon dioxide produced by these catalysts appears to result from a secondary water-gas reaction. With iron catalysts, carbon dioxide is the chief oxygenated product, and the usage ratio and carbon dioxide formation are more dependent upon gas composition and flow than with nickel, cobalt, and ruthenium catalysts. Available data indicate that at least a sizable fraction of the carbon dioxide formed on iron catalyst may result from a secondary water-gas reaction. At all synthesis temperatures, the thermodynamics of the reaction favors the formation of carbon dioxide.

The free energies of synthesis reactions that produce alcohols and other oxygenated molecules are considerably more positive than those of reactions producing hydrocarbons. Thus, it is likely that oxygenated hydrocarbons result from either a primary reaction of hydrogen and carbon monoxide or a reaction of synthesis gas and olefins (the oxo reaction), but not from hydration of olefins.

With cobalt catalysts only small amounts of oxygenated hydrocarbons are produced at atmospheric pressure. Larger amounts of oxygenated organic compounds are formed in the middle-pressure synthesis. For example, Pichler [23] stated that about 1 per cent of the reaction water was oxygenated organic compounds. In Table 24 [64] are presented product distribution data for a cobalt catalyst operated in the middle-pressure range. Alcohols are the principal oxygenated organic compounds, but small amounts of other compounds are present. With $2H_2$:1CO gas, smaller amounts of alcohols and olefins were produced than with $1H_2$:1CO gas, and with both gases the quantity of alcohols decreased with increasing temperature.

With iron catalysts more alcohols and olefins were produced with $1H_2$:1CO gas than with $2H_2$:1CO, as shown in Table 25.[64] Data shown in Table 26 [64] for alcohol and olefin formation from tests of an iron catalyst at 12 atm and 240°C, at different space velocities, are somewhat erratic. Olefin content increased with flow, but it is doubtful if the increase was more than the limits of experimental error. Similarly, the data for the production of alcohols showed no significant trend. However, pilot-plant data on precipitated iron catalysts (Table 36, Chapter

TABLE 24. PRODUCTS FOR COBALT-THORIA-KIESELGUHR CATALYST IN MIDDLE-PRESSURE RANGE (PRESUMABLY 12 ATM) [a]

(0.2 per cent K_2O in catalyst.)

Temperature, °C	Contraction, per cent	Yield, g per cu m	Per Cent Paraffins (>320°C)	Composition of Various Boiling Ranges					
				195°–250°C		250°–320°C		320°–450°C	
				Per Cent Olefins	Per Cent Alcohols	Per Cent Olefins	Per Cent Alcohols	Per Cent Olefins	Per Cent Alcohols
$2H_2$:1CO gas									
160	55	97	53	12	15	9	..	9	25
170	..	93	69	10	10	6	9	3	5
180	72	138	58	10	8	3	3	3	3
$1H_2$:1CO gas									
170	47	71	49	29	27	19	21	17	17
175	50	96	58	33	29	19	23	14	17
195	62	115	54	38	19	23	8	16	8

[a] A. Scheuermann; see reference 64.

TABLE 25. DISTRIBUTION OF PRODUCTS FROM AN IRON CATALYST IN MIDDLE-PRESSURE RANGE [a]

(Space velocity = 240.)

	$2H_2$:1CO	$1H_2$:1CO
Temperature, °C	245	240
Liquids + solids, g per cu m	75	80
C_1–C_5, g per cu m	24	14
Product composition, per cent		
To 195°C	23	18
195°–320°C	24	20
320°–450°C	25	18
>450°C	26	42
Olefins, per cent		
195°–250°C	24	50
250°–320°C	16	44
320°–450°C	8	22
Alcohols, per cent		
195°–250°C	9	27
250°–320°C	6	27
320°–450°C	9	10

[a] A. Scheuermann; see reference 64.

Table 26. Variation in Product Distribution with Space Velocity (Iron Catalyst) [a]

($1H_2$:1CO gas at 12 atm and 240°C.)

Space velocity	240	480	720	960	2,400
CO conversion, per cent	46	34	24	23	11
Liquids + solids, g per cu m	80	61	43	41	12
C_1–C_5, g per cu m	14	8	6	6	10
Product composition, per cent					
To 195°C	18	17	9	5	21
195°–320°C	20	21	20	19	20
320°–450°C	18	23	21	21	24
>450°C	44	39	50	55	35
Olefins, per cent					
To 250°C	50	51	57	57	54
250°–320°C	44	42	42	49	46
320°–450°C	32	25	30	33	37
Alcohols, per cent					
To 250°C	27	29	19	23	30
250°–320°C	27	23	16	22	30
320°–450°C	10	13	8	15	19

[a] A. Scheuermann; see reference 64.

4) indicated that the yields of alcohols plus olefins at constant temperatures increased with recycle ratio, *ie*, with linear velocity of recycle gas. Lower operating temperatures increased the fraction of alcohols but decreased the fraction of olefins, as shown in Table 27.[64] In these experiments the conversion was maintained constant, and the flow and temperatures were increased. Pressure favored the formation of oxygenated hydrocarbons and decreased the production of olefins (Table 28).[64]

The only important differences between the usual Fischer-Tropsch and synol processes are that higher space velocities and lower temperatures are used in the synol process, and the synol products are characterized by large fractions of alcohols and olefins. The analyses of synol products of Reisinger [79] (Tables 42 and 43 of Chapter 4, pp 392 and 395) indicate that large amounts of alcohols and olefins are found in all carbon number fractions. The mole fraction of alcohols in each carbon number fraction varied from 15 to 40 per cent from C_2 to C_8, increased from 40 to 65 per cent from C_8 to C_{11}, and remained at 60 to 65 per cent above C_{11}, as shown in Figure 66. Fewer moles of methanol were produced than of ethanol and propanol. Synol alcohols, at least up to C_9, have been shown to be chiefly primary, straight-chain alcohols. Products from some iron catalysts contain as much as 10

[79] Dr. Reisinger, T.O.M. Reel 13, Bag 3,043, Item 3.

TABLE 27. VARIATION OF PRODUCTS FROM AN IRON CATALYST WITH TEMPERATURE [a]

($2H_2$:1CO gas at 12 atm.)

Space velocity	240	720
Temperature, °C	230	250
CO conversion, per cent	64	60
Liquids + solids, g per cu m	70	45
C_1–C_5, g per cu m	18	37
Product composition, per cent		
To 195°C	22	43
195°–320°C	23	29
320°–450°C	23	17
>450°C	32	11
Olefins, per cent		
To 250°C	33	42
250°–320°C	22	29
320°–450°C	12	14
Alcohols, per cent		
To 250°C	22	4
250°–320°C	14	1
320°–450°C	5	1

[a] A. Scheuermann; see reference 64.

TABLE 28. EFFECT OF PRESSURE ON PRODUCTS FROM AN IRON CATALYST [a]

($1H_2$:1CO gas at space velocity of 240.)

Pressure, atm	12	50
Temperature, °C	215	225
CO conversion, per cent	29	30
Liquids + solids, g per cu m	56	48
C_1–C_5, g per cu m	3	12
Product composition, per cent		
To 195°C	17	41
195°–320°C	12	28
320°–450°C	21	17
>450°C	30	12
Olefins, per cent		
195°–250°C	48	23
250°–320°C	48	20
320°–450°C	36	18
Alcohols, per cent		
195°–250°C	16	57
250°–320°C	18	57
320°–450°C	27	43

[a] A. Scheuermann; see reference 64.

per cent of esters. Aldehydes and ketones are usually present in amounts less than 1 per cent.[71] Small amounts of organic acids are produced in the synthesis with iron catalysts.[80] Iron catalysts in fluidized reactors at temperatures above 300°C and pressures of 20 atm or higher produce large amounts of oxygenated organic compounds.[81] This oxygenated

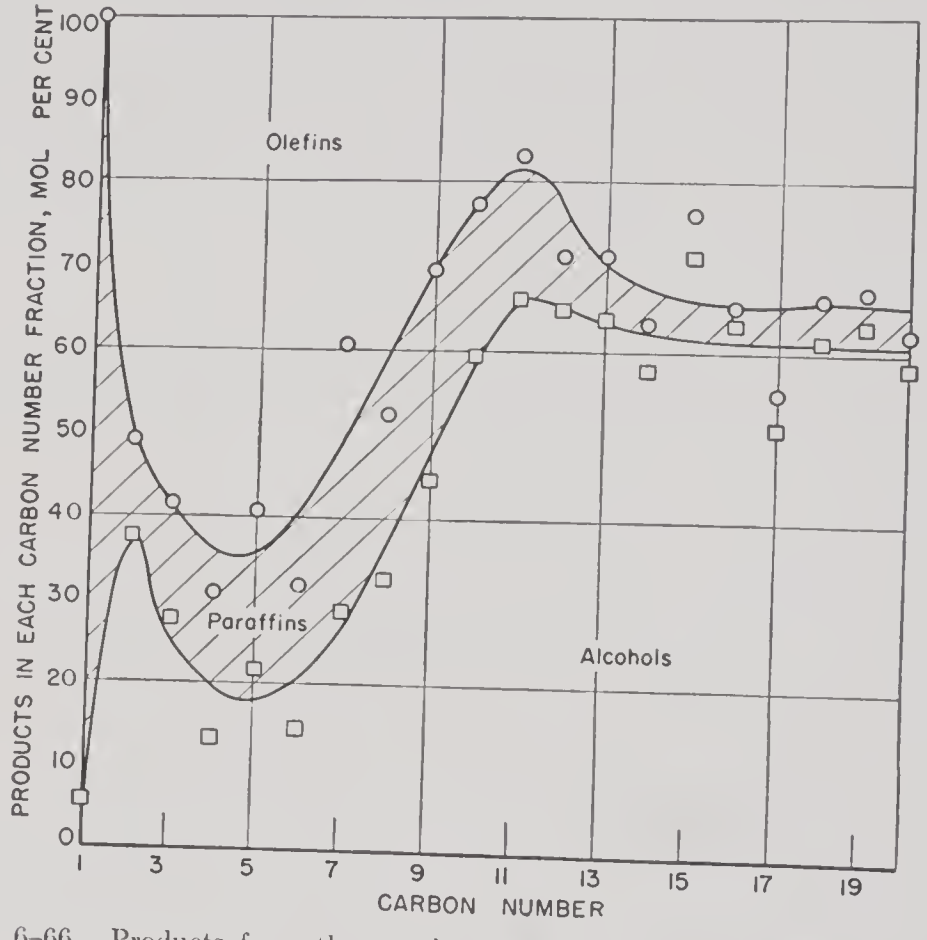


FIGURE 6–66. Products from the synol process, mole per cent paraffins, olefins, and alcohols in each carbon number fraction. From data of reference 79.

material is about 25 per cent of the product (exclusive of water, carbon dioxide, and gaseous hydrocarbons). About 75 per cent of the oxygenated product was soluble in the reaction water. As shown in Table 64 of Chapter 4, the water-soluble fraction was composed of 52 per cent alcohols, 27 acids, 10 aldehydes, and 11 ketones. The oil-soluble oxygenated material comprised 33 per cent alcohols, 34 aldehydes plus ketones, and 33 acids. Ethanol, acetaldehyde, acetone, and acetic acid were the major constituents of the water-soluble alcohol, aldehyde, ketone, and acid fractions, respectively.

[80] H. Pichler, private communication.

[81] A résumé of a paper of T. Q. Eliot, C. S. Goddin, and B. S. Pace, *Petroleum Processing*, **4**, 676 (1949).

Thus, the production of oxygenated compounds was favored by low temperature, high space velocity, high operating pressure, and carbon monoxide-rich synthesis gas. Alcohol yields showed a maximum at ethanol and then decreased with increasing carbon number. The small yield of methanol was probably the result of the low value of the equilibrium constant for methanol formation (Table 7, p 21, of Chapter 1). The products from fluid reactors indicated that large amounts of oxygenated material could be produced at high space velocities and at temperatures greater than 300°C. Hence, it appears that the production of alcohol was more dependent upon space velocity than upon temperature.

DISTRIBUTION OF HYDROCARBON PRODUCTS

The overall distribution of hydrocarbons from cobalt catalysts at 1 and 7 atm is illustrated by the data of Underwood [82] in Figure 67.

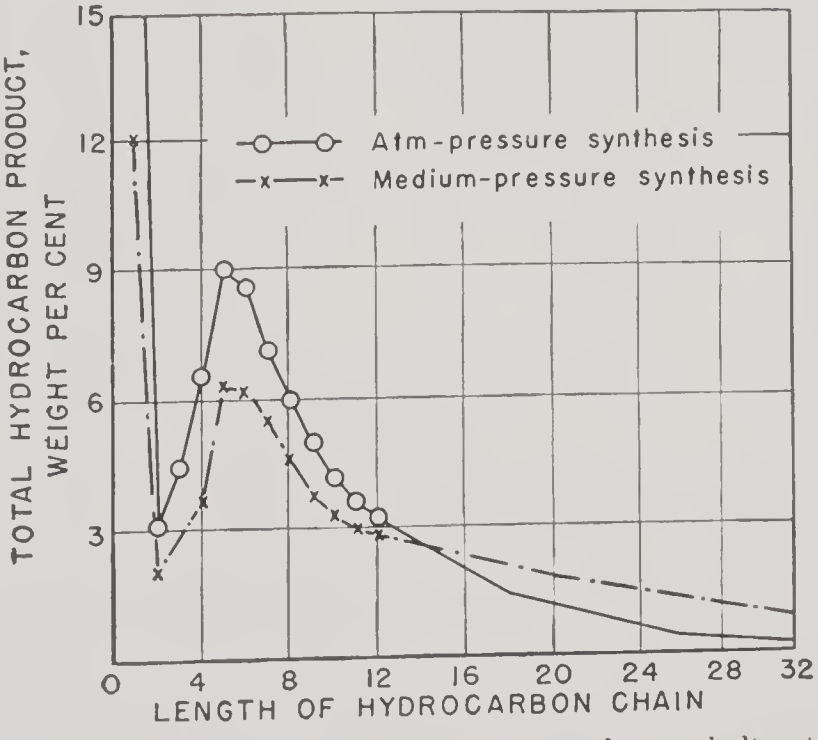


FIGURE 6–67. Distribution of hydrocarbon products from cobalt catalysts in the atmospheric- and medium-pressure syntheses. Reproduced by permission from reference 82.

Distribution curves for cobalt catalyst are usually characterized by high yields of methane, low yields of C_2 hydrocarbons, and increasing amounts of hydrocarbons with increasing carbon number to a maximum at C_5. Distribution curves of other workers (*cg* Figures 72 and 74)

[82] A. J. V. Underwood, *Ind. Eng. Chem.*, **32**, 449 (1940).

varied considerably but showed the above characteristics. An increase in operating pressure increased the average molecular weight of the hydrocarbon products. This was also shown by the data of Fischer and Pichler [51] in Table 1 of Chapter 4, in which the average molecular weight increased to a maximum at 15 atm.

Complete distribution data for the products from iron catalysts are not available. This is possibly due to the difficulties inherent in fractional distillation and analysis of materials containing fairly large amounts of oxygenated compounds. The C_1–C_4 hydrocarbons from iron catalysts showed a minimum at C_2, but the relative amounts of C_2 hydrocarbons were greater than for cobalt catalysts, as shown in Table 29.[83] The average molecular weight of products from iron

TABLE 29. GASEOUS PRODUCTS FROM IRON CATALYSTS [a]

($1H_2$:1CO gas at 7.8 atm.)

Catalyst	Hydrocarbon Products							
	C_1	C_2		C_3		C_4 [b]		C_5 [b]
	g per cu m	g per cu m	Per Cent Olefin	g per cu m	Per Cent Olefin	g per cu m	Per Cent Olefin	Per Cent Olefin
Fused Fe_3O_4-MgO-K_2O	13.8	8.6	22.1	14.3	76.8	8.0	79.4	77.7
Precipitated Fe_2O_3-CuO-K_2CO_3	6.2	5.6	41.0	8.7	82.4	2.7	77.4	72.0

[a] R. A. Friedel and R. B. Anderson; see reference 83.

[b] Sizable amounts of C_4 and C_5 hydrocarbons were probably dissolved in liquid and solid hydrocarbons.

catalysts increased with pressure up to about 20 atm (Table 30; see also Table 5 of Chapter 4) but decreased somewhat at higher pressures (Table 28). With iron catalysts, the average molecular weight of the products decreased with space velocity (Table 26). This is also shown in the distribution data of Reisinger [79] for products from the synol process (high space velocity, low-temperature operation). Here the maximum mole per cent and weight per cent of total products (exclusive

[83] R. A. Friedel and R. B. Anderson, *J. Am. Chem. Soc.*, **72**, 1,212, 2,307 (1950).

TABLE 30. EFFECT OF OPERATING PRESSURE ON BOILING RANGE OF PRODUCT FROM AN IRON CATALYST [a] (RUHRCHEMIE, GERMANY)

	Pressure, atm		
	1	5	20
CO conversion, per cent	95	70	75
Total yield, g per cu m	90	86	120
Gasoline, per cent [b]	57	30	22
Diesel oil, per cent [b]	24	25	22
Wax, per cent [b]	19	45	56
Olefins in gasoline, per cent	68	63	63
Olefins in Diesel oil, per cent	41	49	46

[a] E. H. Reichl; see reference 71.

[b] Per cent of total of gasoline, Diesel oil, and wax.

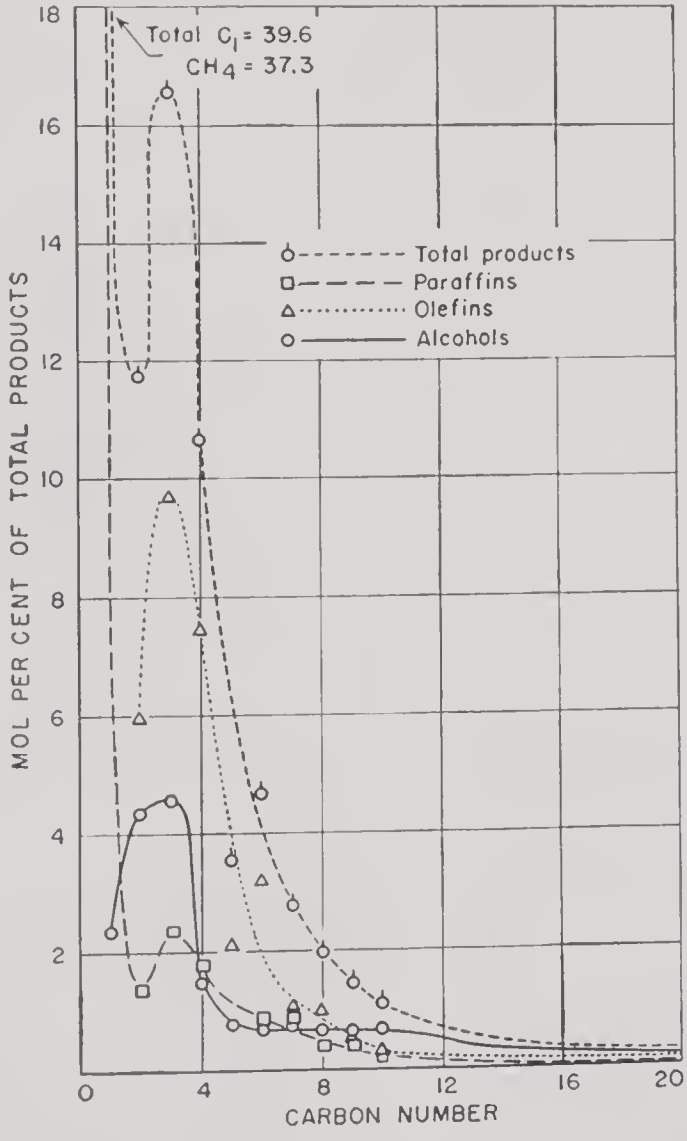


FIGURE 6–68. Distribution of the products from the synol process, mole per cent of total products. Reproduced from reference 79.

of C_1), paraffins, olefins, and alcohols, were observed at C_3, as shown in Figure 68. The fraction of C_2 products was again smaller than C_3, but the amount of ethylene was greater than ethane. The yields of methane were very large.

With cobalt catalysts (Table 24), the yield of solid paraffins was greater with $2H_2$:1CO gas than with $1H_2$:1CO gas. However, with iron catalysts (Table 25), the fraction of light hydrocarbons was greater

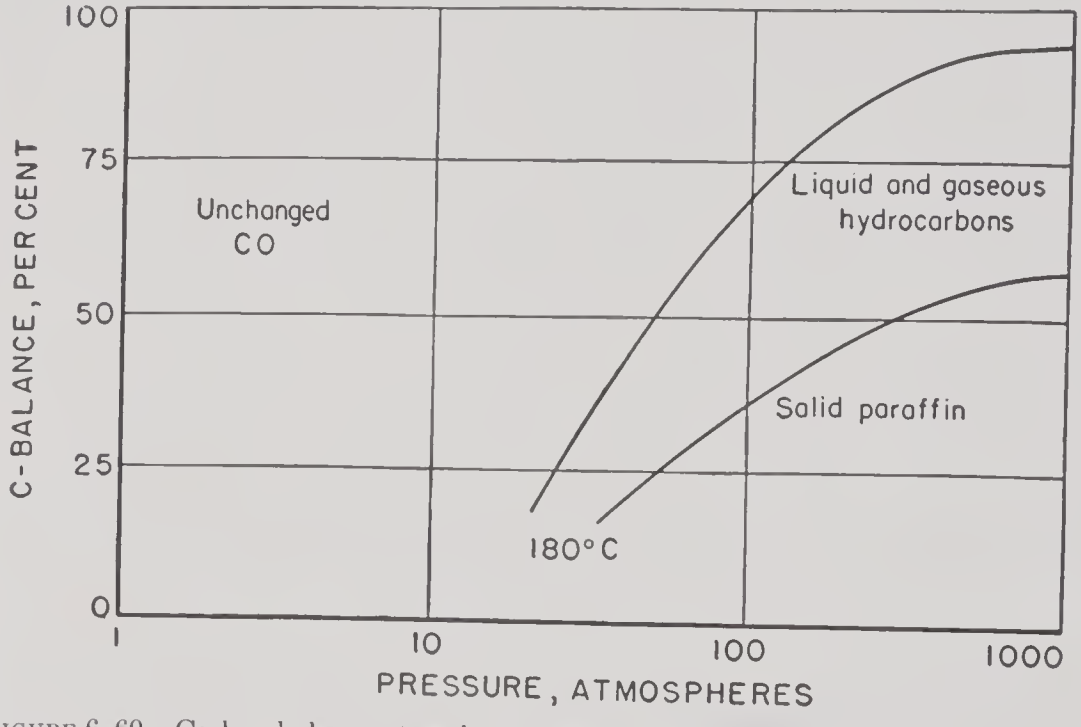


FIGURE 6–69. Carbon balance at various pressures on a ruthenium catalyst. Reproduced from reference 78.

with $2H_2$:1CO gas than with $1H_2$:1CO. With nickel, cobalt, and iron catalysts, the average molecular weight of the product decreased with temperature.

With ruthenium catalysts[78] the average molecular weight of the hydrocarbon products increased with pressure up to the highest pressure used. The distribution between solid and liquid-plus-gaseous hydrocarbons is shown in Figure 69. More than 50 per cent of the wax from tests of ruthenium catalyst at 1,000 atm had a melting point higher than 120°C. The molecular weight of these high-melting waxes was greater than 3,000

The tendency to form olefins increases from nickel to cobalt to iron catalysts. Many of the factors that tend to increase or decrease the olefin content are the same for catalysts of these three metals. The fraction of unsaturated hydrocarbons increased with the flow of syn-

thesis gas, as shown by Murata, Ishikawa, and Tsuneoka [84] (Figure 70) in tests of nickel catalysts. With iron catalysts, the increase of the fraction of olefins with flow was small, as shown by the data of Table 26. However, the recycle experiments with iron catalysts (Table 36 of Chapter 4) indicated that the olefin content increased with flow. Also the products from the synol process (Figures 66 and 68) contained a large fraction of olefins which very likely resulted from operation at a high space velocity. The hydrocarbon fractions from iron catalysts in fluidized reactors at high space velocities and temperatures above 300°C

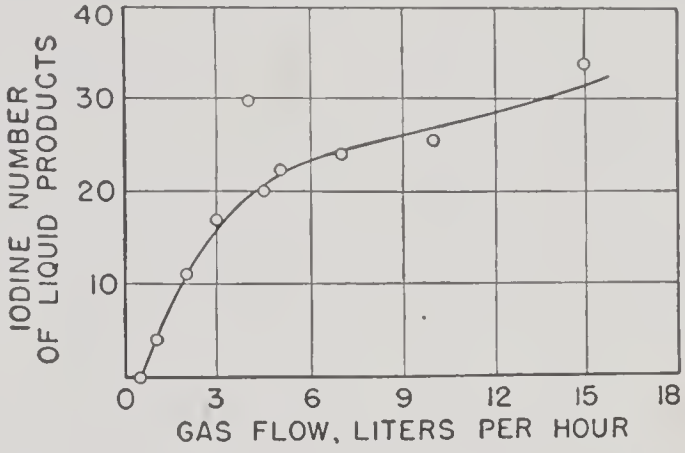


FIGURE 6–70. The unsaturation of products from a nickel catalyst as a function of space velocity. Reproduced from reference 84.

usually contained more than 80 per cent olefins. In this case both the high space velocity and temperature favored olefin formation. The data of Anderson, Krieg, Friedel, and Mason,[45] in which the ratio of saturated to unsaturated hydrocarbons of the C_4 fraction was plotted against bed length (or reciprocal of space velocity), in Figure 71, showed that with $2H_2$:1CO and $3.5H_2$:1CO gas the fraction of olefins decreased with bed length. With $3.5H_2$:1CO gas, the ratio of H_2:CO increased as the gas passed down the catalyst bed, and this probably explains the large increase in the fraction of saturated hydrocarbons with bed length. With $1H_2$:1CO gas the ratio of hydrogen:carbon monoxide decreased with bed length and the fraction of olefins increased with bed length. Thus, olefin production is a function of gas composition as well as bed length (or space velocity). Extrapolation of these curves to zero bed length indicated that both saturated and olefinic hydrocarbons are obtained in the primary reaction. Tables 24 and 25 also show that the fraction of olefins in products from cobalt and iron catalysts increased with decreasing ratios of H_2:CO.

[84] Y. Murata, S. Ishikawa, and S. Tsuneoka, *J. Soc. Chem. Ind. Japan*, Suppl. binding, **39**, 329 (1936).

With cobalt catalysts, the fraction of olefins did not change appreciably with temperature (Table 24), but with iron catalysts (Table 27) the fraction of olefin increased with temperature. The fraction of olefins from cobalt catalysts decreased with operating pressure.[85] With

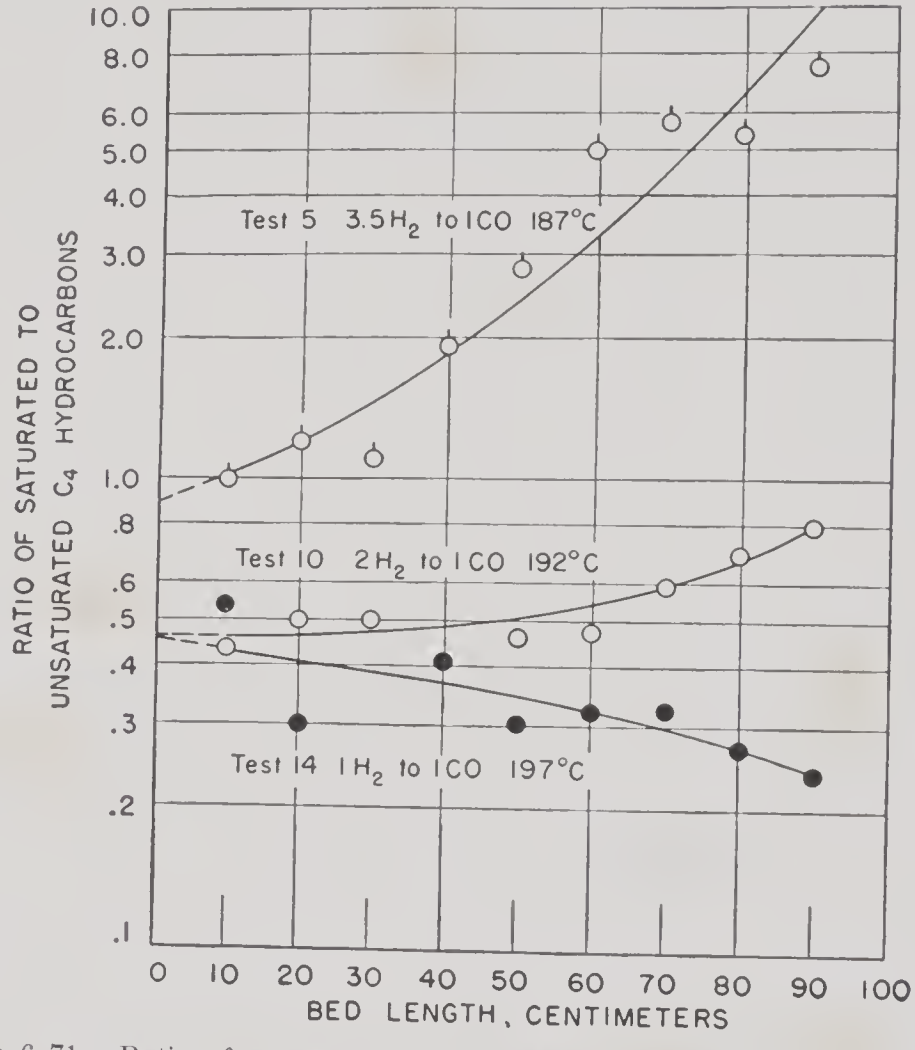


FIGURE 6-71. Ratio of saturated to unsaturated C_4 hydrocarbons—bed length curves for tests 5, 10, and 14 with $3.5H_2$ to 1CO, $2H_2$ to 1CO, and $1H_2$ to 1CO gas, respectively. The ratios of C_4 hydrocarbons were computed from the total amounts of these components present at any given position in the bed, and are not differential values. Reproduced by permission from reference 45.

iron catalysts the percentage of olefins decreased slightly with pressure up to 20 atm (Table 30) and to a greater extent from 12 to 50 atm (Table 28).

The fraction of olefins in the products from cobalt catalysts in the C_2, C_3, C_4, and C_5 fractions was 0 (none detectable), 39, 47, and 43 per cent, respectively.[83] Above C_5 the olefin fraction decreased with

[85] H. H. Storch *et al.*, *U. S. Bur. Mines Tech. Paper* 709 (1948), p 130.

molecular weight. In the products from iron catalysts (Table 29) ethylene was present in sizable amounts, but ratio of olefin to paraffin was smaller for C_2 than for the C_3–C_5 fractions.

HYDROCARBON ISOMERS IN FISCHER-TROPSCH PRODUCTS

Fischer-Tropsch hydrocarbons contain predominantly straight-chain isomers. According to an estimate of von Weber,[86] the fraction of branched isomers in the C_6, C_8, and C_{10} hydrocarbon fractions obtained from cobalt catalysts was 0.15, 0.27, and 0.40, respectively. In products from cobalt catalysts, Koch and Hilberath [87] found that the butane fraction contained 92.5 per cent *n*-butane and 7.5 per cent isobutane, and they showed qualitatively the presence of monomethyl paraffin isomers in the C_5–C_7 range. Traces of more highly branched isomers were reported, but none involving quaternary carbon atoms.

Friedel and Anderson [83] reported mass spectrometric analyses of C_5–C_8 paraffin isomers from atmospheric-pressure tests of cobalt catalysts, as shown in Table 23 of Chapter 4. The straight-chain isomer predominated in each fraction, and the extent of branching increased with carbon number. Only monomethyl branched isomers were found.

Infrared spectrometric analysis of the C_6–C_8 olefins from cobalt catalysts indicated (Table 24 of Chapter 4) a greater fraction of internal double-bond isomers than α-isomers, the fraction of α-olefins decreasing with molecular weight. Transconfigurations were found in greater concentrations than *cis* forms of internal olefins.

Preliminary analyses of products from iron catalysts at 7.8 atm indicated the presence of straight-chain and monomethyl paraffin isomers; however, the percentage of branched isomers was greater than in products from cobalt catalysts. Olefins were predominantly α rather than internal double-bond isomers.

Recently, Bruner [88] described the isomers present in the products of the synthesis on iron catalysts in a fluidized reactor (the Hydrocol process). Complete mass spectrometric data were reported for the C_3, C_4, and C_5 fractions, as shown in Table 59 of Chapter 4. A sample of the liquid product was hydrogenated to saturated hydrocarbons, and the C_6, C_7, and C_8 fractions analyzed for extent of branching, by a mass spectrometric method. These data, combined with those of Table 61 of Chapter 4, are presented in Table 31. As was observed in the

[86] V. von Weber, *Angew. Chem.*, **52**, 607 (1939).
[87] H. Koch and F. Hilberath, *Brennstoff-Chem.*, **22**, 135, 145 (1941); **23**, 67 (1942).
[88] F. H. Bruner, *Ind. Eng. Chem.*, **41**, 2,511 (1949).

products from cobalt catalysts, the extent of branching increased with molecular weight, but the fraction of branched isomers was larger than that in the products from cobalt catalysts. Small amounts of dimethyl isomers and cyclic hydrocarbons were found. Hydrocarbons containing quaternary carbon atoms were not observed. The carbon number fractions from C_4 to C_{11} contained from 85 to 90 per cent olefins, which were shown to be predominantly α-olefins.

Table 31. Extent of Branching of Hydrocarbon Products from Iron Catalysts in a Fluidized Reactor [a]

	Weight Per Cent			
	Normal	Monomethyl	Dimethyl	Cyclic
C_4	89.4	10.6	...	0.0
C_5	80.9	18.8	0.0	0.3
C_6	75.9	20.0	0.4	3.7
C_7	60.2	29.3	1.7	8.8
C_8	55.4	36.6	2.4	5.6

[a] F. H. Bruner; see reference 88.

Weitkamp [89] (Table 62 of Chapter 4) presented isomer analyses of products from fluidized iron catalysts which are in accord with the data of Bruner. In addition, the aromatic hydrocarbons were analyzed in detail. For example, in the C_8 fraction, ethyl benzene, *o*-xylene, *m*-xylene, and *p*-xylene were found in this order in decreasing amounts (Table 63 of Chapter 4).

Straight-chain isomers are less stable thermodynamically than most of the corresponding branched isomers. Thus, straight-chain isomers must be produced by primary processes rather than by subsequent isomerization of other isomers. Olefins are unstable thermodynamically, with respect to hydrogenation or hydrocracking, and are probably produced by primary processes. α-Olefins are usually less stable thermodynamically than olefins with internal double bonds. The analyses of Friedel and Anderson [83] and Bruner [88] indicated the presence of larger amounts of α-olefins than the amounts expected for equilibrium with internal double-bond isomers.

The Mechanism of the Fischer-Tropsch Synthesis

The mechanism of heterogeneous catalytic reactions may be divided into five steps: (*a*) transport of reactants to the surface, (*b*) adsorption, (*c*) reaction on the surface, (*d*) desorption of products, and (*e*) transport

[89] A. W. Weitkamp, *Ind. Eng. Chem.*, to be published.

of products from the surface. The slowest of these determines the kinetics, and step *c*, as well as subsequent reactions, determines the distribution of products. Mass transfer of reactants to or of products from the catalyst particles is probably not rate-controlling in the Fischer-Tropsch synthesis because the temperature dependence of the rate is considerably greater than that usually expected for diffusional processes. However, mass transfer in the pores of the catalyst particles as a rate-determining step cannot be excluded on this basis. Mass transfer in the pores of Fischer-Tropsch catalysts is probably not a simple process, since the pores are at least partially filled with adsorbed hydrocarbons during synthesis.

Adsorption of hydrogen or carbon monoxide on iron, cobalt, and nickel catalysts is rapid at synthesis temperatures. Hydrogen is probably largely adsorbed as atoms and carbon monoxide as molecules which may react with other carbon monoxide molecules to form carbide. However, adsorption data are not complete, since almost all the experiments reported in the literature were made with only one gaseous component and with no adsorbed hydrocarbon on the catalyst.

Rate equations involving desorption of products or intermediates as a rate-determining step have been shown to approximate the kinetic data for cobalt and possibly also nickel catalyst. With iron catalysts, the available kinetic data may be approximated by equations in which the rate-controlling step is the adsorption of hydrogen. The Fischer-Tropsch synthesis is a *very slow* catalytic reaction; hence, either the catalytic process is very slow or only a very small fraction of the surface participates in the reaction.

Most discussions of the Fischer-Tropsch reaction mechanism are concerned with the reactions at the catalytic surface, step *c*. Early studies of the synthesis led to the consideration of carbides as intermediates on the basis of the following observations: (*a*) only metals that form interstitial carbides are active in the synthesis; (*b*) these catalysts are active at temperatures at which the carbides are stable; and (*c*) the rates of carbide formation and synthesis are somewhat similar. The synthesis of higher hydrocarbons on ruthenium catalysts as reported by Pichler [78] in 1940 is an exception to these generalizations, since ruthenium apparently does not form carbides at synthesis temperatures in either carbon monoxide or synthesis gas.

The carbide hypothesis was first suggested by Fischer and Tropsch [1] in 1926. It was postulated that carbides formed by the synthesis gas are hydrogenated to methylene groups. These polymerize to form hydrocarbon chains that desorb from the surface as saturated and unsaturated hydrocarbons.

THE CARBIDE THEORY OF CRAXFORD AND RIDEAL

Craxford and Rideal [30] presented a more detailed carbide theory in which the following steps were postulated:

$$Co + CO \rightarrow Co{-}CO \text{ (chemisorption)} \qquad (A)$$

$$Co{-}CO + CO \rightarrow Co{-}C \text{ (surface carbide)} + CO_2 \text{ or} \qquad (B)$$

$$Co{-}CO + H_2 \rightarrow Co{-}C \text{ (surface carbide)} + H_2O \qquad (C)$$

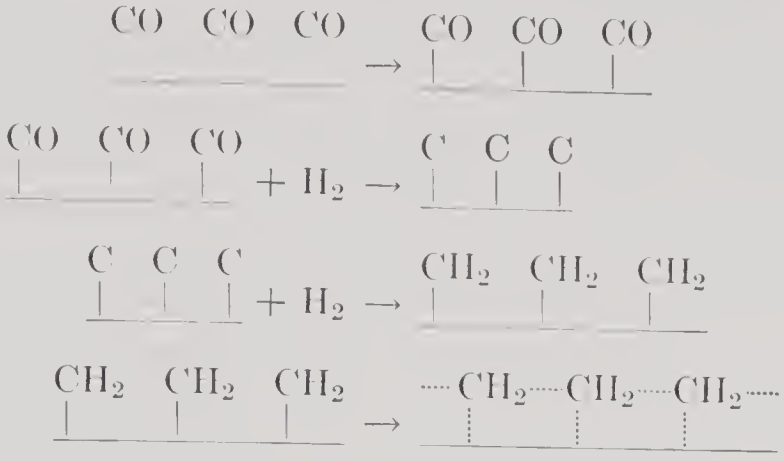
$$Co{-}C + H_2 \rightarrow Co{-}CH_2 \rightarrow \text{higher hydrocarbons} \qquad (D)$$

With cobalt catalysts, reaction *C* must predominate over reaction *B*, since water, the chief oxygenated product, cannot be formed by subsequent reactions.

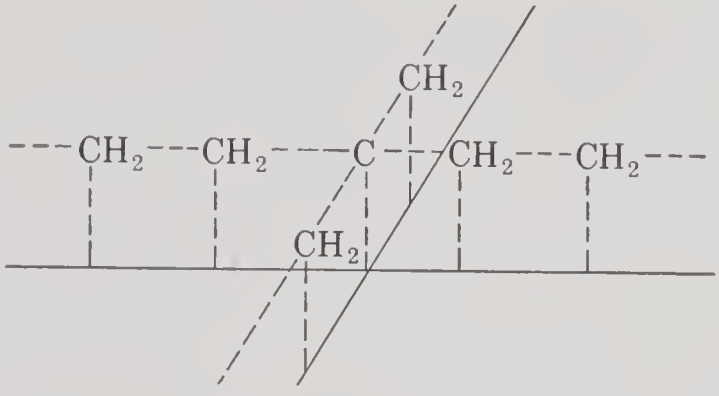
To elucidate the reaction mechanism, the conversion of *para-* to *ortho*-hydrogen in *para*-hydrogen-carbon monoxide mixtures was studied on cobalt catalysts. The experimental results were summarized as follows: [30]

> While the Fischer synthesis is proceeding at about 200°C, the ortho-para-conversion does not occur to any marked extent, but it does occur for the following conditions under which either there is no reaction or else methane is being formed.
>
> (i) With normal synthesis, $CO + H_2$, at temperatures below 140°C, in which case there is no reaction.
>
> (ii) With synthesis gas at 200°C for the first hr or so, during which time methane and cobalt carbide are being produced and no oil.
>
> (iii) With a mixture of 24 H_2 to CO at 200°C even after 24 hr. With this gas mixture hardly any oil is formed, only methane.
>
> (iv) With synthesis gas above 250°C. Again methane is the product and no oil.

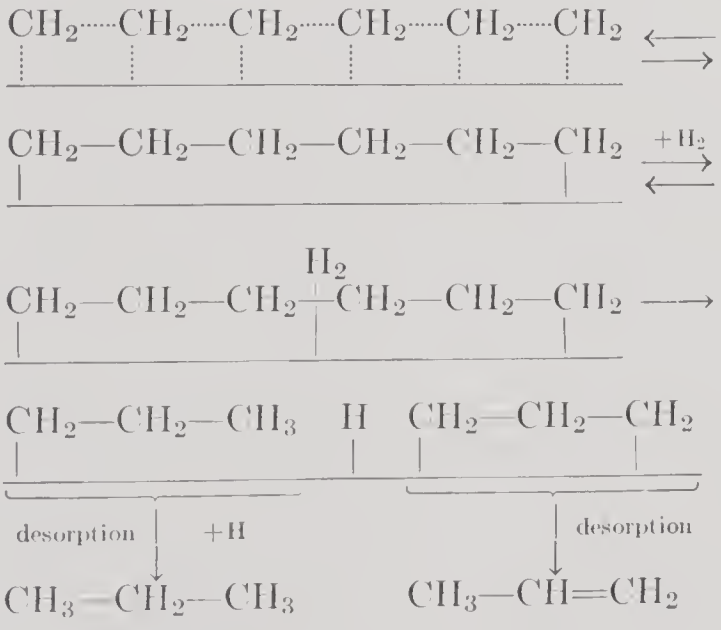
Since very little *para* to *ortho* conversion occurred during the synthesis of oil, Craxford and Rideal concluded that no appreciable amount of atomic hydrogen was present in the normal synthesis, and that methane production involved atomic hydrogen in some stage of the reaction. Inhibition of the *para-ortho* conversion was related to the rather complete coverage of the surface with cobalt carbide that was postulated for the state of the catalyst in the normal synthesis. A detailed mechanism involving only molecular hydrogen was presented for the formation of macromolecules on the catalyst surface:



Branched macromolecules with quaternary carbon atoms may be formed by incorporation of a carbon atom into chains of methylene groups.



The macromolecules increase in size until split by hydrogen.



A pseudo-equilibrium was postulated between polymerization of methylene groups and hydrocracking, the latter reaction being favored by high concentrations of chemisorbed hydrogen. Hydrocracking of the

macromolecules may follow the dissociative chemisorption mechanisms postulated by Taylor and coworkers [90] (see p 73, Chapter 2).

In a later paper, Craxford [52] postulated that carbon dioxide was produced by the water-gas reaction, and methane and gaseous hydrocarbon formation by hydrocracking. These reactions occurred on bare cobalt atoms and in the presence of atomic hydrogen; the normal synthesis

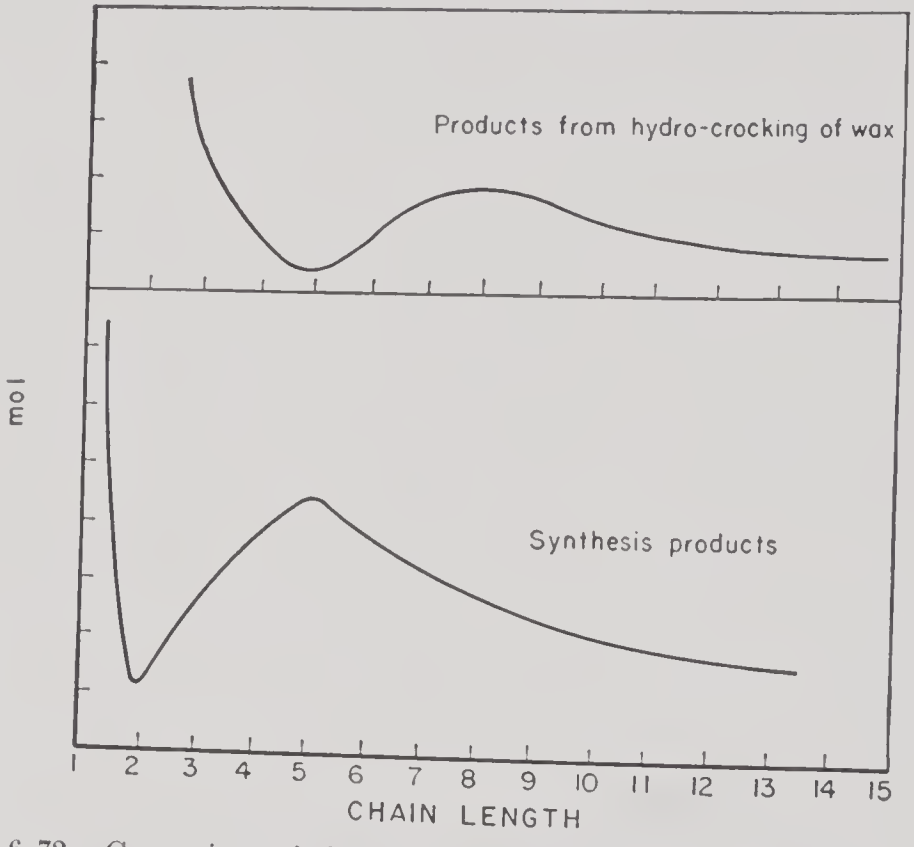


FIGURE 6–72. Comparison of the products formed by hydrogenation of a used cobalt catalyst with those formed in the synthesis. Reproduced by permission from reference 40.

occurred on a surface of cobalt carbide. In another paper, Craxford [40] studied the hydrocracking of wax deposited in a cobalt catalyst in atmospheric-pressure synthesis at 185°C. The distribution of products from hydrocracking at 185°C is compared in Figure 72 with the distribution from the synthesis at this temperature. The general shape of the distribution curves was similar, but the minimum and maximum of the distribution from the hydrocracking were shifted to longer chain lengths. For the first 3 hr, the rate of hydrocracking was greater than the rate of synthesis. Craxford concluded that this was evidence that the synthesis products were produced by hydrocracking of macromolecules. Data presented for the incorporation of methane (p 504) were taken

[90] K. Morikawa, W. S. Benedict, and H. S. Taylor, *J. Am. Chem. Soc.*, **58**, 1,445, 1,795 (1936); K. Morikawa, N. R. Trenner, and H. S. Taylor, *ibid.*, **59**, 1,103 (1937).

as evidence for the dissociative adsorption of hydrocarbons on the catalyst surface, the adsorbed methane participating in the polymerization-depolymerization equilibrium.

The theory of Craxford was the first attempt to formulate the mechanism of the synthesis in a detailed manner, and it has proved to be a powerful stimulus to discussion and experimental studies of the reaction mechanism. Many aspects of the theory may be adversely criticized, especially in the light of experimental data that have become available since Craxford's theory was published. These are as follows:

1. The experimental data of Craxford and Rideal [30] are not as conclusive as may be desired.

2. The fact that *ortho-* to *para*-hydrogen conversion does not occur to a large extent in the normal synthesis does not necessarily preclude the presence of hydrogen atoms on the catalyst surface. It may merely indicate that hydrogen molecules converted to the equilibrium concentration of *ortho-para* forms do not escape from the surface in sizable amounts. This could occur in at least two cases: (*a*) if the rate of adsorption of hydrogen is the rate-determining step, and (*b*) if the rate of diffusion in long, small pores is an important factor in the synthesis. In the latter instance, hydrogen molecules desorbed from the surface of a pore would have to diffuse against a net flow of gas into the pore caused by the gas contraction. Thus, it is possible that, under certain conditions, very little of the desorbed hydrogen would appear in the exit gas, and that most of this hydrogen remains in the pores until it reacts in the synthesis.

3. The amount of cobalt carbide found in used Fischer-Tropsch catalysts is quite small. Carburization of cobalt catalysts to produce high concentrations of carbide caused the catalyst to be inactive (p 525), and operation of reduced catalysts at atmospheric pressure in $1H_2:1CO$ or gases richer in carbon monoxide caused a progressive decrease in activity. Carbon monoxide-rich gas should favor carbide formation. Inhibiting the ability of the catalyst to form carbide by deposition of free carbon (p 526) did not change the activity in the synthesis. However, it should be mentioned that the low activity of catalysts carburized in carbon monoxide may be due to poisoning of the active surface by oxide formation, and the activity of catalysts carburized with higher hydrocarbons should be investigated.

4. With iron catalysts, Hägg and hexagonal (Fe_2C) carbides are found in sizable amounts in used catalysts, and in some cases the activity increases with the fraction of iron present as Fe_2C carbides. Herbst [19] concluded that the presence of the hexagonal carbides was a necessary but not a sufficient requirement for high catalytic activity. However,

only carbide in the surface layers can be directly involved in the reaction mechanism, but the bulk carbide may provide a suitable substrate for active surface layers.

5. Branched hydrocarbons formed in the synthesis contain ternary rather than quaternary carbon atoms as predicted by Craxford's theory.

6. With cobalt catalysts, reactions producing methane and carbon dioxide occur to an appreciable extent throughout the catalyst bed, and Craxford's theory does not appear to be an adequate explanation of the data of Anderson, Krieg, Friedel, and Mason [45] and Koelbel and Engelhardt.[53]

7. The carbide theory does not predict the formation of oxygenated compounds. Iron catalysts which usually contain rather large amounts of bulk Fe_2C carbides produce very much greater amounts of oxygenated products than cobalt catalysts.

8. The distribution curves of products from synthesis and hydrocracking differ sufficiently to make their interpretation questionable.

9. Incorporation of methane in the synthesis supports the postulates of dissociative adsorption of hydrocarbons on the catalyst and the polymerization-depolymerization equilibrium of Craxford. However, it should be noted that incorporation of methane is not a general phenomenon and possibly occurs only with specially prepared catalysts or in short periods of the catalyst life. Analysis of synthesis and product gas mixtures for methane by simple volumetric methods is not very accurate. Careful experiments of Emmett and Kummer,[41] employing tracer techniques as described later in this section, indicate that methane was not incorporated in the synthesis.

10. The rate of the reaction between hydrocarbons adsorbed on cobalt catalysts and hydrogen is markedly different if carbon monoxide is present or absent; the rate of hydrocracking with pure hydrogen is several times the rate of synthesis. This suggests that the hydrocracking reaction may be inhibited by poisoning of the catalyst with carbon monoxide. This poisoning may be due to carbide as suggested by Craxford, chemisorbed carbon monoxide, or some intermediate derived from carbon monoxide. Similarly, cobalt catalysts operated in carbon monoxide-rich gas or those precarbided in carbon monoxide have low catalytic activity. Thus, some surface phase derived from carbon monoxide appears to poison the catalyst, and it is possible that the selectivity of the catalyst in the synthesis is due to a partially poisoned surface. The slow rate of the synthesis is consistent with the concept of a partially poisoned catalyst. If this is correct, the surface phase formed in the presence of carbon monoxide should be regarded as an inhibitor and not the active catalyst as suggested by Craxford.

MECHANISM STUDIES USING C^{14}

Kummer, DeWitt, and Emmett [27] studied the mechanism of the Fischer-Tropsch synthesis on iron and cobalt catalysts, using the radioactive isotope of carbon, C^{14}, as a tracer. Only a small fraction (0.1 per cent or less) of radioactive carbon monoxide, $C^{14}O$, in ordinary carbon monoxide was necessary for accurate measurement. The radioactivity of reactants and products was determined with a Geiger counter by the following method: The reactants and products were fractionated into three portions, the first containing H_2, CO, and CH_4; the second, CO_2 and gasol hydrocarbons (C_3 and C_4); and the third, higher hydrocarbons. These fractions were analyzed by combustion in oxygen to carbon dioxide and water. The carbon dioxide was absorbed in a barium hydroxide solution, and the precipitated barium carbonate was collected on a filter paper and dried. The radioactivity of this barium carbonate was determined with a Geiger counter.

The catalysts were tested in the synthesis at about atmospheric pressure in an all-glass apparatus in which synthesis gas or other gases were circulated by a magnetic pump (this system was somewhat similar to that of Weller [32] in Figure 15, Chapter 2). Surface areas of the catalysts were determined by the nitrogen adsorption method, and the extent of metal in the catalyst surface was estimated by the chemisorption of carbon monoxide at −78°C. Catalysts studied were (*a*) pure fused magnetite, (*b*) fused Fe_3O_4-Al_2O_3-SiO_2-ZrO_2, (*c*) precipitated Co-ThO_2-kieselguhr, and (*d*) precipitated iron oxide gel.

At first consideration, the experimental test of the carbide theory appears to be simple. The catalyst should be carbided with a surface layer containing C^{14} carbide, and the rate of appearance of C^{14} in the hydrocarbon products should indicate the extent to which the carbide participates in the synthesis. However, it must first be established whether or not exchange reactions between radioactive carbon as carbide and the carbon atoms in carbon monoxide, carbon dioxide, and hydrocarbons occur, and, second, whether a uniform and stable surface of C^{14} carbide can be formed.

To minimize the use of C^{14}, the reduced catalyst was carburized with normal carbon monoxide to 60–70 per cent Fe_2C or Co_2C, and then the catalyst was carburized an additional 10 per cent with carbon monoxide containing $C^{14}O$. The radioactivity of the surface was determined by hydrogenating the equivalent of carbide covering about 25 per cent of the catalyst surface and determining the radioactivity of the methane. In all cases, even though carbide containing C^{14} equivalent to many layers was deposited on the catalyst, the radioactivity of the surface

was smaller than that of the carbon monoxide used in the second stage of the carburization. In hydrogenation of these carbided catalysts over long periods, some radioactivity was found in the methane formed until all the carbon was removed. This suggests that some of the C^{14} diffuses rapidly through the iron phase and deposits on the interface of Fe_2C crystallites at rather large distances from the surface. On hydrogenation, the C^{14} together with normal carbon diffuses to the surface. Although the activity of the surface was lower than anticipated, its activity did not change appreciably over periods as long as 48 hr at 305°C.

It was established that hydrocarbons did not exchange with C^{14} carbide. Exchange between carbon monoxide and C^{14} carbide was about 5 per cent at 250°C and 29 per cent at 322°C. A catalyst that had been converted to 65 per cent normal Fe_2C was operated in the synthesis at 253°C with $1H_2$:1CO gas to which about 20 per cent of methane containing $C^{14}H_4$ had been added. Radioactivity was not observed in either the gasol or liquid hydrocarbon fractions, indicating no exchange between methane and synthesis products and *no incorporation of radioactive methane*. This is important because some radioactive methane is produced by partial hydrogenation of radioactive carbide in the synthesis.

In the synthesis experiments, the radioactivity of the surface was determined before and after the synthesis by brief hydrogenations. The average activity was assumed to be the mean of these two values. Data obtained in a typical experiment are given in Table 32. In this test, the

Table 32. Fischer-Tropsch Run (Run 108) on Catalyst B Carbided to 94.7 Per Cent Fe_2C

(Weight of reduced sample, 1.95 g; temperature of run, 252°C; time of run, 332 min; pressure of run, 765–580 mm; surface activity before the run, 1,410 counts per min per cc; surface activity after the run, 745 counts per min per cc; synthesis gas contained 82.2 cc H_2 and 80.1 cc CO.)

Produced or Left, cc		Activity	Unaccounted for, cc	
CO	45.5	4.7 counts per min per cc of CO_2	C [a]	16.1
H_2	22.2		H_2	16.7
CH_4	5.1	199 " " " " " " "	O_2	2.75
CO_2	3.02			
$C_{2.6}H_5$	3.98	45 " " " " " " "		
H_2O	23.1			

Per cent of total product formed through Fe_2C as an intermediate $\dfrac{(45)(100)}{(1{,}410 + 745)\ 2} = 4.2$ per cent

[a] The volume that the carbon atoms would occupy if they were an ideal monatomic gas.

radioactivity in the gasol ($C_{2.6}H_5$) fraction indicated that only 4.2 per cent of this product was produced with Fe_2C as an intermediate. A sizable amount of radioactive methane was produced, presumably by direct reduction of the carbide. The synthesis experiments with iron catalysts at 250°C or lower or with cobalt catalysts at 200°C indicate that on the average 10 per cent of the reaction proceeds by the carbide mechanism. These data were based on the radioactivity found in the gasol fraction. Analysis of some of the liquid hydrocarbons showed a somewhat greater radioactivity than the gasol hydrocarbons, indicating that the carbide mechanism may occur to a slightly greater extent in the formation of the liquid hydrocarbons.

The influence of possible surface heterogeneity on the interpretation of these experiments was considered. It might be assumed that hydrocarbons were produced by the carbide mechanism and that 3 or 4 per cent of the surface synthesized 90 per cent of the hydrocarbon. This 3 or 4 per cent of the surface would soon be depleted of radioactive carbide so that 90 per cent of the reaction products would be formed from normal carbide deposited on the catalysts from normal synthesis gas. From such an experiment it might be erroneously concluded that 90 per cent of the reaction occurred by mechanisms other than carbide reduction. Experiments with iron catalysts were arranged in which the amount of reaction, if it proceeded entirely by the carbide mechanism, would involve only a small fraction of the surface. These data, shown in Figure 73, indicated that, when as small a fraction as 1 per cent of the surface was involved, only 11.5 and 15 per cent of the reaction on iron catalysts at 260° and 300°C proceeded by reduction of carbide.

Kummer, DeWitt, and Emmett [27] concluded that only a small fraction of the hydrocarbons is formed by the reduction of bulk or "surface" carbide, the term "carbide" in this case referring to any carbide deposited on the catalyst by carbon monoxide. These experiments surely do not preclude carbon atoms that may exist momentarily at the catalyst surface in some reaction step being intermediates in the synthesis.

Thermodynamic studies of Hägg carbide, Fe_2C, and cementite of Emmett and coworkers [91] (Chapter 1, p 30) indicated that it is not possible to hydrogenate these carbides to appreciable amounts of any olefin or to paraffins above butane. However, it is thermodynamically possible to incorporate carbidic carbon with hydrogen and carbon monoxide into the synthesis. Recent studies of Podgurski, Kummer, DeWitt, and Emmett [22] showed that carbon monoxide is not adsorbed on Fe_2C (Hägg) carbide at 100° and 200°C, whereas hydrogen is appre-

[91] J. T. Kummer, L. C. Browning, and P. H. Emmett, *J. Chem. Phys.*, **16**, 739 (1948); L. C. Browning, T. W. DeWitt, and P. H. Emmett, *J. Am. Chem. Soc.*, **72**, 4211 (1950).

ciably chemisorbed. Since the chemisorption of carbon monoxide is probably a necessary step in the reaction mechanism, it appears that Fe_2C cannot be an active catalyst in the synthesis.

To summarize our discussion of the carbide theory: The results of thermodynamic, tracer, and synthesis studies indicate that bulk-phase carbide participates in the synthesis only to a negligible extent, if at all. Hydrogenation of "surface" carbide, as formed by precarbiding catalysts

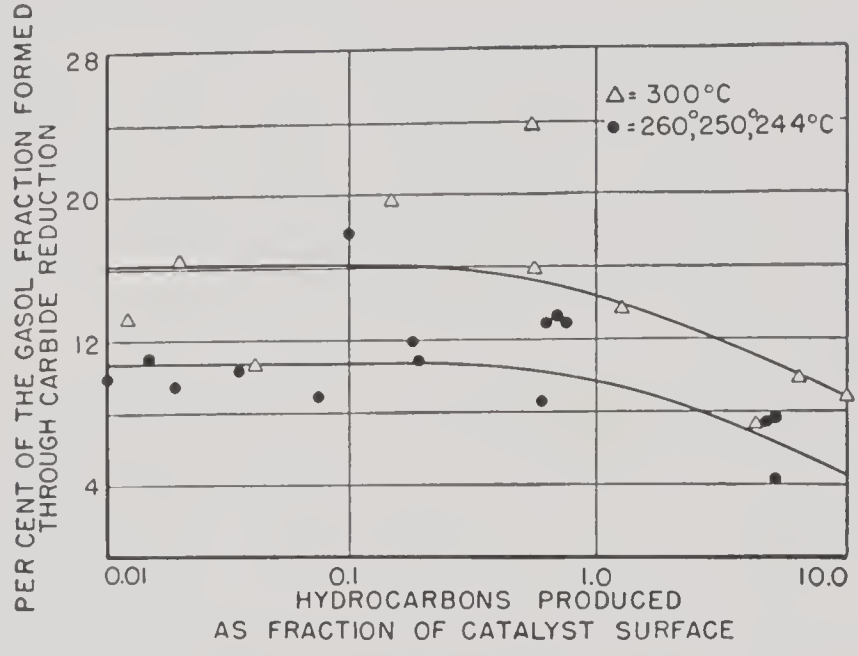


FIGURE 6–73. The per cent of the synthesis proceeding by the carbide mechanism as a function of the fraction of the surface involved in the reaction. Reproduced by permission from reference 27.

with carbon monoxide, can account for only 10–20 per cent of the hydrocarbon product. However, the mechanism may include a step in which carbon atoms are momentarily formed at the surface, but it is questionable if these should be termed surface carbides. Probably "chemisorbed carbon" would be preferable. A number of the postulated of Craxford's detailed reaction mechanism have been shown to be contrary to experimental evidence as summarized on pp 571–575. Synthesis experiments indicate that cobalt carbide is not an active catalyst in the synthesis. Adsorption studies may possibly indicate that carbides of iron are also inactive in the synthesis,[22] but this is contradictory to a large number of data in which the activity of iron catalysts is increased by pretreatment to form hexagonal or Hägg carbides, cementite, or nitrides. It is possible that the presence of interstitial carbon or nitrogen atoms in iron catalysts may enhance the activity in a relatively secondary manner, such as by increasing the resistance of the catalyst to oxidation during the synthesis.

POSSIBLE MECHANISMS WHICH DO NOT INVOLVE SURFACE CARBIDE AS AN INTERMEDIATE

The reaction mechanism need not involve the hydrogenation of adsorbed carbon monoxide to carbide and methylene groups. The mechanism may involve the formation of formaldehyde which may undergo hydrogenation and condensation to compounds containing more than one carbon atom, as postulated for the higher alcohol synthesis. The small amount of formaldehyde in the reaction products may be explained on a thermodynamic basis. The presence of oxygenated organic molecules in the reaction products is not conclusive evidence against carbide as an intermediate since oxygenated compounds can be formed by an oxo-type reaction involving olefins produced by an initial reaction. However, the presence of methyl and ethyl alcohols as found in products from iron catalysts cannot be explained in this manner.

Pichler [23] stated:

> The possible occurrence of intermediate compounds of the carbonyl-type should not be arbitrarily discarded. . . . Optimum conditions (for the synthesis) prevail at pressures just below which (at the corresponding temperatures) the tendency toward formation of volatile carbonyls becomes so great that deterioration of the catalyst results. In other words, conditions must be chosen in such a way that the rate of formation of volatile carbonyl remains somewhat less than that for the supposed intermediate carbon monoxide compounds with hydrogen.

A comparison of the optimum pressure of synthesis with the minimum pressure at which deleterious carbonyl erosion of the catalyst occurs is given in Table 33. Pichler's hypothesis is not a unique explanation of

Table 33. Comparison of Optimum Synthesis Pressures with Pressures at Which Undesirable Formation of Carbonyls Occurs at Synthesis Temperatures [a]

	Synthesis Gas Pressure, atm			
Active Component	Ni	Co	Fe	Ru
Optimum for synthesis	1	5–30	10–30	100–1,000
Undesirable carbonyl formation	>1	>30	>30	Carbonyls may form on the surface of the catalyst under these conditions of temperature and pressure

[a] H. Pichler; see reference 23.

the observed results, since any reaction mechanism in which the rate increases with pressure would give this type of relationship. In the synthesis with cobalt catalysts, it is possible that most of the advantages

of middle- over atmospheric-pressure operation may result from relatively secondary phenomena (see p 522). However, the suggestion that the initial attachment of carbon monoxide to catalyst surface involves carbonyl-type bonds appears very reasonable.

There are some interesting similarities between the Fischer-Tropsch and higher-alcohol syntheses. In the latter, the distribution of alcohols shows a minimum at C_2. Complete analyses of the products of the higher-alcohol synthesis have not been published, but available data (p 109, Chapter 2) indicate that only normal, monomethyl, and dimethyl substituted carbon chains are present. Alcohols with quaternary carbon atoms have not been reported. In both syntheses, the presence of alkali oxides increases the average molecular weight of the product.

HYPOTHESES REGARDING THE METHOD OF BUILDING THE CARBON CHAIN

In the remainder of this section on the reaction mechanism we shall discuss hypotheses regarding the method of formation of the molecules found in the synthesis products without particular consideration of the initial step of the process, and conclude with a detailed set of postulated reactions, which are consistent with the observed products from the synthesis.

The Polymerization-Depolymerization Hypothesis

Craxford (p 572) postulated a polymerization-depolymerization mechanism involving the formation and hydrocracking of macromolecules at the catalyst surface. Montgomery and Weinberger [92] considered the possibility of explaining the observed product distribution by a thermodynamic polymerization-depolymerization equilibrium. Equilibrium calculations were made by a modification of the Brinkley method.[93] Methane and ethane were assumed to be the independent components, and products were expressed in terms of equations of the type

$$\cdot(n-1)C_2H_6 = C_nH_{2n+2} + (n-2)CH_4 \qquad (7)$$

The equilibrium distributions were expressed in terms of temperature, methane:ethane ratio, and overall atom ratio of hydrogen:carbon of the products. Qualitative agreement with distribution data was obtained at 200°C with $CH_4:C_2H_6 = 11.5$ and $H:C = 2.67$. However, the values of the $CH_4:C_2H_6$ ratio and the H:C ratio required to approximate the distribution curve were considerably greater than those usually

[92] C. W. Montgomery and E. B. Weinberger, *ibid.*, **16**, 424 (1948).
[93] S. R. Brinkley, Jr., *ibid.*, **14**, 563 (1946); **15**, 107 (1947).

observed. The observed values of $CH_4:C_2H_6$ ratio usually vary from 5 to 8; the ratio of H:C = 2.67 requires a usage ratio of H_2:CO of 2.33, which is higher than usually observed. Better agreement with the distribution data of products obtained at 200°C was found if the temperature used in the calculation was taken as 327°C, and $CH_4:C_2H_6$ = 7.0, and H:C = 2.59. The authors suggested that the surface temperature of the catalyst may actually be considerably higher than the bed temperature.

The method of Montgomery and Weinberger [92] fairly satisfactorily approximates the distribution of products from cobalt catalyst; however, it should be noted that specification of the $CH_4:C_2H_6$ and H:C ratios places strong limitations on the distribution curve. It does not appear that this method would be applicable to products containing sizable amounts of olefins or oxygenated compounds, since these should not be found in appreciable amounts if thermodynamic equilibrium between the products is attained.

Hypotheses Involving Stepwise Addition to Carbon Chain

Herington [94] considered a stepwise increase of the carbon chain on the catalyst surface rather than the hydrocracking of macromolecules postulated by Craxford. Each carbon number fraction was given a probability β_n of appearing as product rather than growing on the surface to appear as a higher-molecular-weight hydrocarbon. The surface concentration of these molecules was assumed to be sufficiently great so that the number appearing as product did not upset the concentration on the surface. Thus, $\beta_n = \phi_n / \sum_{n+1}^{\infty} \phi_i$, where ϕ_n is the number of moles of product of carbon number n. The values of β_n, computed from the distribution of products from cobalt catalysts of Craxford, were fairly constant at 0.30. Friedel and Anderson [83] computed values of β_n from a more complete and somewhat different distribution curve of products from cobalt catalysts at atmospheric pressure, as shown in Figure 74. The values of β_n increased from less than 0.10 for C_2 to greater than 0.35 for C_{20}. From C_5 to C_{15}, β_n was about 0.20 with a slight upward trend. It has been shown by Friedel and Anderson that, when the value of β_n is constant, $1 + \beta = \phi_n / \phi_{n+1}$. Thus, with respect to the number of moles in a given carbon number fraction, x,

$$\phi_n = \phi_x (1 + \beta)^{-(n-x)} \tag{8}$$

and

$$W_n \cong 14 n \phi_n = 14 n \phi_x (1 + \beta)^{-(n-x)} \tag{9}$$

[94] E. F. G. Herington, *Chemistry & Industry*, 1946, 347.

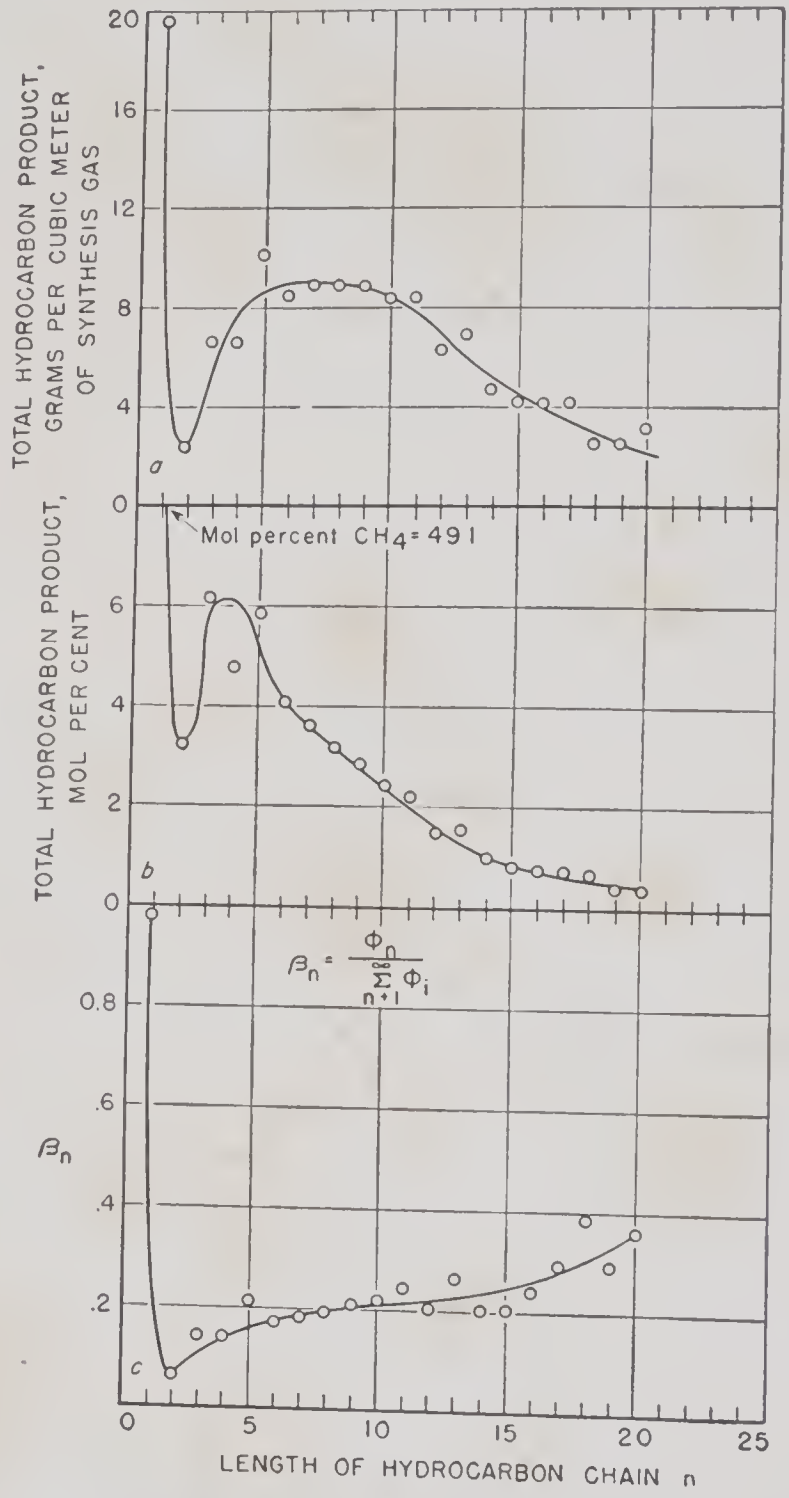


FIGURE 6–74. Parts *a* and *b* present the distribution of total hydrocarbon products from atmospheric tests of cobalt catalysts at 190°C in terms of grams per cubic meter of synthesis gas and mole per cent. Part *c* is a plot of Herington's probability term βn. Constructed from data of reference 83.

where W_n is weight of product of carbon number n. This weight curve has a maximum at $1/n = 2.303 \log_{10} (1 + \beta)$, *eg*, for $\beta = 0.20$ the maximum is predicted at the C_5 and C_6 fractions.

Weller and Friedel [95] considered the process of building molecules by successive, one-step additions to the carbon chain of groups containing a single carbon atom, and demonstrated that with simple and reasonable assumptions it was possible to predict accurately the percentage of each isomer in the carbon number fractions from C_5 to C_8 of products from cobalt catalysts. It is not necessary to specify the type of the group added to the carbon chain. The postulated rules for the addition were:

1. "Addition occurs at any terminal or next to terminal (penultimate) carbon atom with two restrictions:

   a. Addition to a tertiary carbon atom does not occur.

   b. Addition to a side chain occurs only if the side chain is attached to a penultimate carbon.

2. "The probability of addition to a terminal carbon atom (*a*) is intrinsically different from that for addition to a penultimate one (*b*)," and $a + b = 1$. "All terminal atoms have the same *a priori* probability, as well as all penultimate atoms," and these probabilities are independent of chain length but may depend upon the nature of the catalyst.

3. "The distribution of isomers in the final product is identical with the distribution on the catalyst surface."

Beginning with C_3, it is possible to form *n*-butane in $2a$ ways and *i*-butane in b ways, the fractions of *n*- and *i*-butane being $\frac{2a}{2a + b}$ $\left(= \frac{2a}{a + 1} \right)$ and $\frac{b}{a + 1}$, respectively. Pentanes can be formed by a carbon addition to either *n*- or *i*-butane, *n*-pentane being formed from *n*-butane, and *i*-pentane by addition to both *n*- and *i*-butane. The fractions of *n*- and *i*-pentane are then

$$n\text{-pentane} = \frac{2a}{2a + 2b} \cdot \frac{2a}{a + 1} = \frac{2a^2}{a + 1}$$

$$i\text{-pentane} = \frac{2b}{2a + 2b} \cdot \frac{2a}{a + 1} + \frac{b}{a + 1} = \frac{b(2a + 1)}{a + 1}$$

In this manner the distribution of isomers in any carbon number fraction may be evaluated in terms of a and b. Comparison of observed isomer

[95] S. Weller and R. A. Friedel, *J. Chem. Phys.*, **17**, 801 (1949).

distribution data with those calculated, using empirical values of a and b in Tables 34 and 35, show that this method of predicting product distribution is quite satisfactory.

Table 34. Comparison of Calculated and Observed Percentages of Isomers in Products from Cobalt Catalysts

	Mole Per Cent in Fraction ·		
Isomers	Observed [a]	Weller and Friedel [b] $a = 0.961$, $b = 0.039$	Anderson, Friedel, and Storch [c] $f = 0.035$
n-Butane		98.0	96.6
i-Butane		2.0	3.4
n-Pentane	95.0	94.2	93.4
i-Pentane	5.0	5.8	6.6
n-Hexane	89.6	90.5	90.2
2-Methyl pentane	5.7	5.6	6.4
3-Methyl pentane	4.7	3.8	3.2
Other C_6 isomers	0	<0.1	<0.1
n-Heptane	87.7	87.0	87.3
2-Methylhexane	4.6	5.4	6.2
3-Methylhexane	7.7	7.3	6.2
Other C_7 isomers	0	<0.25	<0.3
n-Octane	84.5	83.6	84.4
2-Methylheptane	3.9	5.2	6.0
3-Methylheptane	7.2	7.1	6.0
4-Methylheptane	4.4	3.5	3.0
Other C_8 isomers	0	<0.25	<0.4

[a] R. A. Friedel and R. B. Anderson; see reference 83.
[b] S. Weller and R. A. Friedel; see reference 95.
[c] R. B. Anderson, R. A. Friedel, and H. H. Storch; see reference 96.

Anderson, Friedel, and Storch [96] proposed a mechanism that predicts the isomer as well as the carbon number distribution of hydrocarbon products. Suppose that the addition of a group containing one carbon atom occurs at the first or the second carbon atom at one end of the chain growing at the surface, and that any subsequent chain growth occurs at this end of the carbon chain. A reaction occurring at one or

[96] R. B. Anderson, R. A. Friedel, and H. H. Storch, *ibid.*, to be published.

TABLE 35. COMPARISON OF CALCULATED AND OBSERVED PERCENTAGES OF ISOMERS IN PRODUCTS FROM IRON CATALYSTS

	Mole Per Cent in Fraction		
Isomers	Observed [a]	Weller and Friedel [b] $a = 0.890$, $b = 0.110$	Anderson, Friedel, and Storch [c] $f = 0.115$
C_4 Normal	89.4	94.2	89.7
Iso	10.6	5.8	10.3
C_5 Normal	81.2	83.8	81.3
Iso	18.8	16.2	18.7
C_6 Normal	78.8	74.6	73.6
Monomethyl	20.8	24.8	25.4
Dimethyl	0.4	0.64	0.97
C_7 Normal	66.0	66.4	66.6
Monomethyl	32.1	31.3	30.7
Dimethyl	1.9	3.3	2.6
C_8 Normal	58.7	59.2	61.5
Monomethyl	36.9	36.0	34.8
Dimethyl	2.5	4.8	4.8

[a] F. H. Bruner; see reference 88.

[b] S. Weller and R. A. Friedel; see reference 95.

[c] R. B. Anderson, R. A. Friedel, and H. H. Storch; see reference 96.

the other carbon atoms of the double bond of an α-olefin with formation by a series of reactions, of an α-olefin containing one additional carbon atom would fill these requirements, but the development is not limited to α-olefins as intermediates. Further assumptions are:

a. The rate of addition to the end carbon may be characterized by a first-order rate constant, α, with respect to the concentration of a species of growing hydrocarbon chain at the catalyst surface.

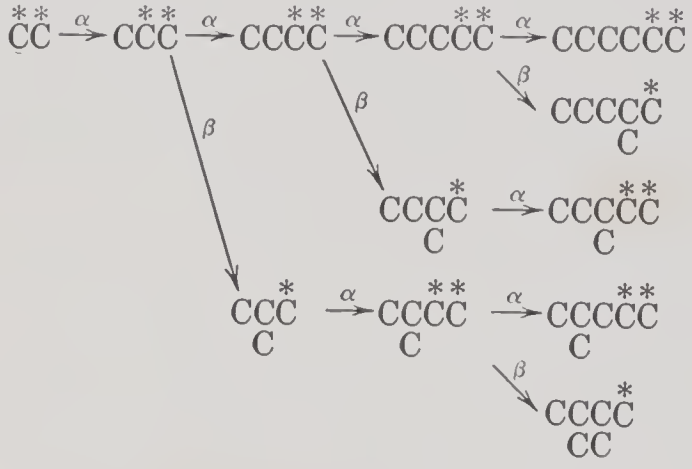
b. The rate of addition to the second carbon atom is characterized by a similarly defined constant, β.

c. Addition does not occur at a carbon atom already attached to three carbon atoms.

d. The rate of appearance of any species in the gas phase, Q_n, is proportional to its concentration on the surface and may be characterized by a first-order constant, γ.

c. The values of these constants do not change with the number or arrangement of carbon atoms in the growing hydrocarbon chain.

Hence, the reaction is postulated to proceed according to the following scheme, where the asterisk indicates the positions at which addition can occur:



For any growing group on the surface, its rate of formation must be equal to its rate of disappearance by either growth to the next higher groups or appearance as product in the gas phase. For normal C_4,

$$\alpha C_3 = \alpha C_4 + \beta C_4 + \gamma C_4 \tag{10}$$

and

$$\frac{C_4}{C_3} = \frac{\alpha}{\alpha + \beta + \gamma} = a \tag{11}$$

where C_3 and C_4 are the concentration of groups with three and four (normal) carbon atoms at the surface, and a is a constant. The ratio of rates of appearance of these species, Q_n, is the same as the ratio of concentrations at the surface, *ie*, $Q_4/Q_3 = a$.

Similarly for iso C_4 (C_4'),

$$\beta C_3 = \alpha C_4' + \gamma C_4' \tag{12}$$

$$\frac{C_4'}{C_3} = \frac{Q_4'}{Q_3} = \frac{\beta}{\alpha + \gamma} = b \tag{13}$$

where b is a constant. Let us define another constant, f, where $f = b/a$, so that $Q_4'/Q_3 = af$. Then it is possible to express the carbon number distribution in terms of a and f, and the isomer distribution in terms

of f. By assigning the rate of appearance of C_2 hydrocarbons the value of $\frac{1}{2}$, the relative rates of appearance becomes:

Carbon Number	Relative Rate of Appearance
2	$\frac{1}{2}$
3	a
4	$a^2(1+f)$
5	$a^3(1+2f)$
6	$a^4(1+3f+f^2)$
7	$a^5(1+4f+3f^2)$
8	$a^6(1+5f+6f^2)$
9	$a^7(1+6f+10f^2)$
n	$a^{(n-2)}\left[1+(n-3)f+\frac{(n-4)(n-5)f^2}{2}\right]$

The low value at C_2 results from the fact that the C_2 group has two effective end carbon atoms. The above series reduces to that of Friedel and Anderson [83] for $f = 0$.

The isomer fractions predicted shown only to C_6 are:

CCCC	$1/(1+f)$	CCCCCC	$1/(1+3f+f^2)$
CCC	$f/(1+f)$	CCCCC	$2f/(1+3f+f^2)$
C		C	
		CCCCC	$f/(1+3f+f^2)$
		C	
CCCCC	$1/(1+2f)$	CCCC	$f^2/(1+3f+f^2)$
		CC	
CCCC	$2f/(1+2f)$		
C			

The two methods of predicting the distribution of isomers [95,96] were compared with isomer analyses for cobalt and iron catalysts. Empirical average values of the constants were computed from the observed isomer distribution, and with these average values the distribution was calculated as shown in Tables 34 and 35. For the products from cobalt catalysts, both methods predict the correct fractions of normal isomers, but the method of Weller and Friedel more closely approximates the fractions of individual monomethyl isomers. With distribution data of products from iron catalysts, both methods satisfactorily approximate the data for normal and monomethyl isomers above C_4. However, the method of Weller and Friedel predicts a considerably lower yield of iso C_4 hydrocarbons than observed. The predicted fractions of dimethyl isomers by both methods are greater than those observed.

Table 36 compares the observed carbon number distribution of products from cobalt catalysts (Figure 74) with that predicted by the method of Anderson, Friedel, and Storch,[96] with $a = 0.850$ and $f = 0.035$, and the agreement is good. This method does not fit the product distribution data of Underwood [82] (Figure 67) in a satisfactory manner in the range of C_2–C_5 hydrocarbons; however, the experimental uncertainties in this distribution curve may be large, *eg*, no experimental point is given for C_3 hydrocarbons on the lower curve.

Table 36. Comparison of Observed and Predicted Product Distribution Data for Products from Cobalt Catalysts [a]

($a = 0.850$, $f = 0.035$.)

Carbon Number	Moles		Carbon Number	Moles	
	Observed	Predicted		Observed	Predicted
2	0.80	0.89	11	0.54	0.52
3	1.53	1.51	12	0.37	0.45
4	1.18	1.33	13	0.38	0.39
5	1.46	1.17	14	0.24	0.34
6	1.01	1.03	15	0.20	0.30
7	0.90	0.90	16	0.19	0.26
8	0.79 [b]	0.79 [b]	17	0.18	0.23
9	0.70	0.69	18	0.17	0.20
10	0.60	0.60	19	0.10	0.17
			20	0.09	0.15

[a] R. B. Anderson, R. A. Friedel, and H. H. Storch; see reference 96.
[b] These values were set equal in the calculation.

An oxo-type reaction occurring on α-olefins obeys the addition rules of Anderson, Friedel, and Storch.[96] Carbon monoxide or groups containing one carbon atom derived from it add to the end or the adjacent carbon atom of the double bond to form an oxygen-containing complex that is eventually hydrogenated to an alcohol which, in turn, dehydrates to form an α-olefin containing one more carbon atom than the starting olefin. A mechanism of this type predicts the formation of alcohols and other oxygenated products higher than C_2 as well as olefinic and paraffinic hydrocarbons and predicts that α-olefins should be present in greater than equilibrium amounts. This series of reactions could start with either ethylene or a C_2 oxygenated intermediate such as ethanol.

However, it should be noted that alcohols do not dehydrate at an appreciable rate at usual Fischer-Tropsch temperatures, even on the best dehydrating catalysts, and in the presence of metal catalysts the course of the decomposition is usually different. Badin [97] studied the

[97] E. J. Badin, *J. Am. Chem. Soc.*, **65**, 1,809 (1943).

decomposition of primary aliphatic alcohols on Raney nickel at 195°–275°C. The decomposition was postulated to proceed according to the following reactions: (*a*) dehydrogenation to the corresponding aldehyde; (*b*) deformylation of the aldehyde to carbon monoxide, hydrogen, and an olefin with one fewer carbon atoms than the alcohol; and (*c*) hydrogenation of the olefin. For example, the products of the decomposition of decanol at 230°C contained 43 mole per cent of *n*-nonane, 36 of nonene, and 21 of *n*-decyl aldehyde. Similarly, Suen and Fan [98] observed that heptaldehyde decomposed to hexene and *n*-hexane on a nickel catalyst at 250°C. Ipatieff and coworkers [99] found that primary alcohols decomposed on nickel catalysts in a similar manner except that chiefly paraffinic hydrocarbons were obtained. The rate of alcohol decomposition decreased with increasing operating pressure. Eidus [100] studied the reactions of methanol and ethanol on a cobalt-thoria-kieselguhr catalyst at atmospheric pressure and 170°–200°C. Hydrogen, carbon monoxide, and gaseous and liquid hydrocarbons were produced in the decomposition of methanol. These liquid hydrocarbons were essentially the same as those formed in the normal synthesis; however, the rate of hydrocarbon production from methanol was considerably lower than from synthesis gas, and the rate increased when hydrogen was added to the methanol. With ethanol, sizable yields of methane were observed, as well as other gaseous and liquid hydrocarbons. Eidus [100] postulated that methanol decomposes to hydrogen and carbon monoxide, and ethanol to hydrogen, carbon monoxide, and methane, and that the hydrogen and carbon monoxide combine by usual synthesis reactions. However, it is not necessary to postulate the formation and subsequent reaction of molecular carbon monoxide to explain the data of Eidus. Groups derived from the alcohol may react directly at the catalyst surface to produce higher hydrocarbons.

Wender, Levine, and Orchin [101] have shown that an oxo reaction can occur with alcohols even where olefin formation by dehydration is impossible. Thus, benzyl alcohol reacted in the oxo synthesis with cobalt to form β-phenylethyl alcohol. Hence, an oxo-type reaction mechanism could involve only alcohol-like groups in the growing chains, and reactions producing olefins and paraffins would be required in the chain-ending steps. The chain-ending steps could involve chiefly reactions such as observed by Badin.[97] Available data suggest that alcohol-like

[98] T. J. Suen and S. Fan, *ibid.*, **65**, 1,243 (1943).

[99] V. N. Ipatieff, G. S. Monroe, L. E. Fischer, and E. E. Meisinger, *Ind. Eng. Chem.*, **41**, 1,802 (1949).

[100] Y. T. Eidus, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, **1943**, 65.

[101] I. Wender, R. Levine, and M. Orchin, *J. Am. Chem. Soc.*, **71**, 4,160 (1949).

intermediates would not dehydrate at an appreciable rate on these catalysts.

Weitkamp [89] proposed a method of predicting the isomer distribution of Fischer-Tropsch products which is similar but not identical in its mathematical details to that of Anderson, Friedel, and Storch.[96] Weitkamp considered the growing hydrocarbon chain to be a free radical and with reasonable assumptions was able to extend the development to explain the types and relative amounts of cyclic and olefin isomers. In this development a C_2 radical was the starting point.

In closing this section on reaction mechanisms, we present a set of equations that explain most of the characteristics of synthesis products. It should be emphasized that these are merely postulated reactions. Present knowledge of the interactions of atoms and molecules at metal surfaces is limited, and it may be naïve even to attempt to formulate these reactions. Nevertheless, these suggestions may be useful in providing a stimulus for further studies of the reaction mechansim.

It is assumed that (*a*) hydrogen is chemisorbed as atoms; (*b*) carbon monoxide is chemisorbed on surface *metal* atoms in a manner similar to that postulated for bonds in metal carbonyls (Chapter 1, p 8); and (*c*) the adsorbed carbon monoxide is partially hydrogenated according to reaction 14. Then chain-building reactions occur in two ways: (*a*) by addition to end carbon atoms (equations 15 and 16), and (*b*) by addition to adjacent-to-end carbons (equations 17 and 18). In these reactions it is postulated that the double bonds between carbon and metal atoms are more resistant to hydrogenation if the carbon atom is also attached to a hydroxyl group. Type *b* growth processes involve partial hydrogenation of the carbon-to-metal bond and proceed according to reactions 17 and 18. Here intermediate α is the same as in reaction 17. Intermediate β may grow by reaction 18 to form a group with a methyl side chain.

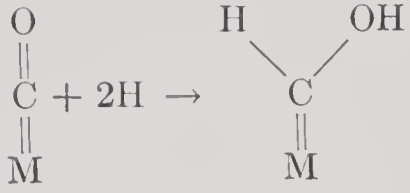
Reactions 19 and 20 illustrate ways of terminating the growth of the chain. According to 19, aldehydes and alcohols may result from desorption and hydrogenation of the alcohol-like groups at the surface. Acids may result from Cannizzaro reactions of these aldehyde-like groups, or by reactions of carbon monoxide with water or alcohols, and esters may be produced by subsequent reactions. Reaction 20, which is based on the decomposition of alcohols on cobalt and nickel catalysts, produces olefins and paraffins.

Reactions 14–20 predict the types of products usually formed in the Fischer-Tropsch synthesis with respect to types of molecules, structure of the carbon chain, and the position of the double bond in olefins. It must be emphasized that these are only hypothetical reactions, and

alternate reactions could be written that would predict the observed products equally well. Although details of the reaction mechanism may be incorrect, two aspects of the mechanism appear to be essentially correct: (*a*) the growing chain involves groups containing oxygen atoms, and (*b*) growth occurs on end or adjacent-to-end carbon atoms of the longest carbon chain, probably at only one end of the growing chain.

The suggested equations are shown below:

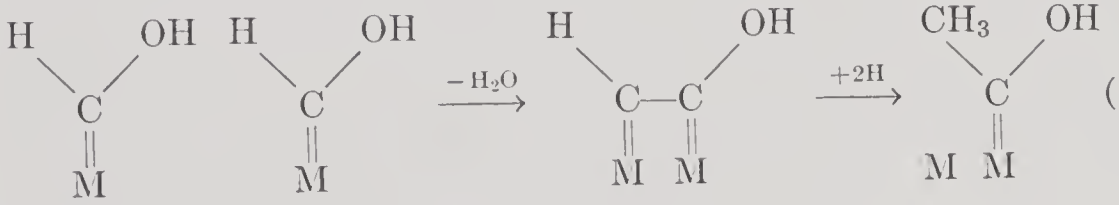
Chain initiation



(14)

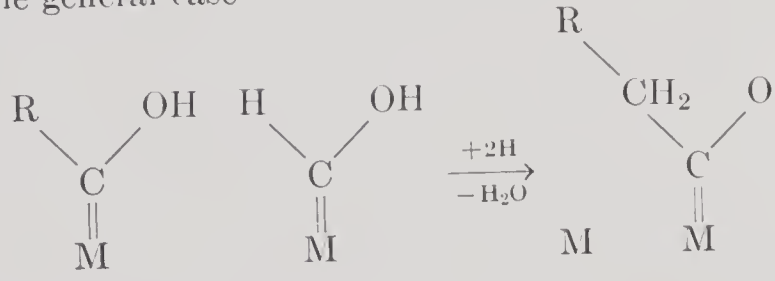
Chain growth

a. At end carbon



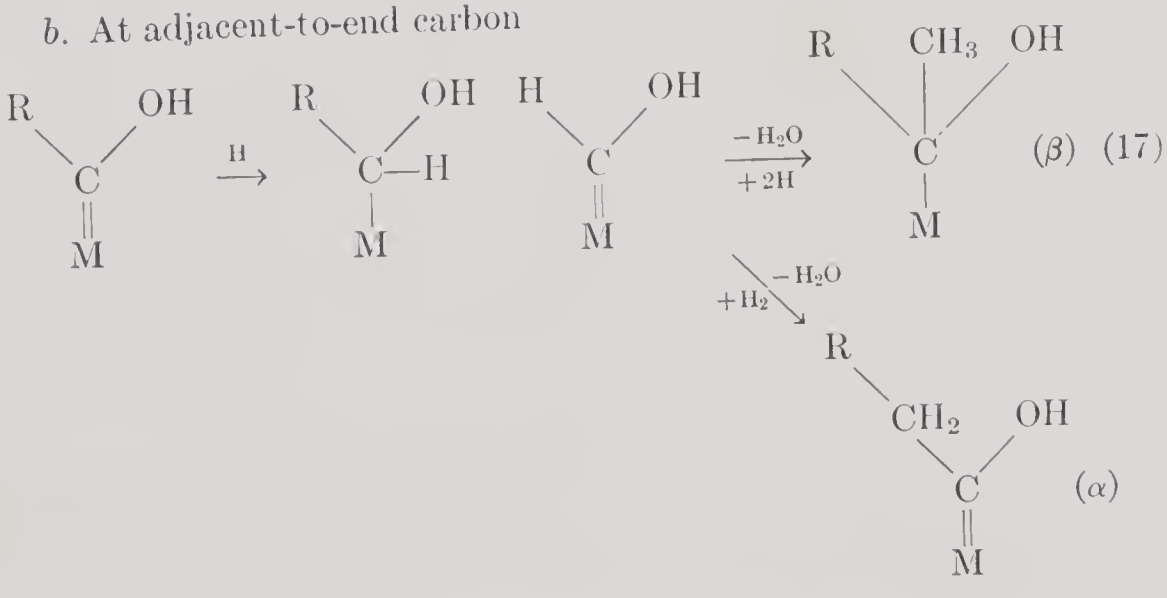
(15)

and for the general case



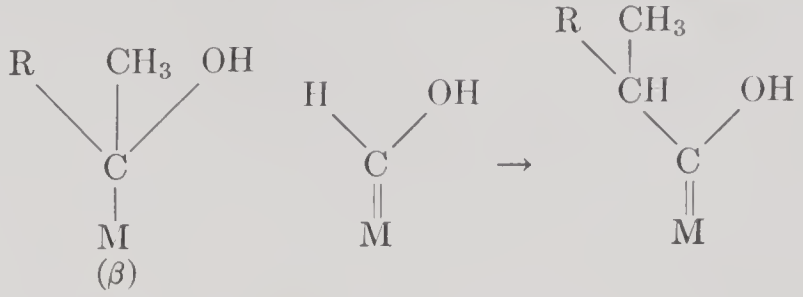
(α) (16)

b. At adjacent-to-end carbon



(β) (17)

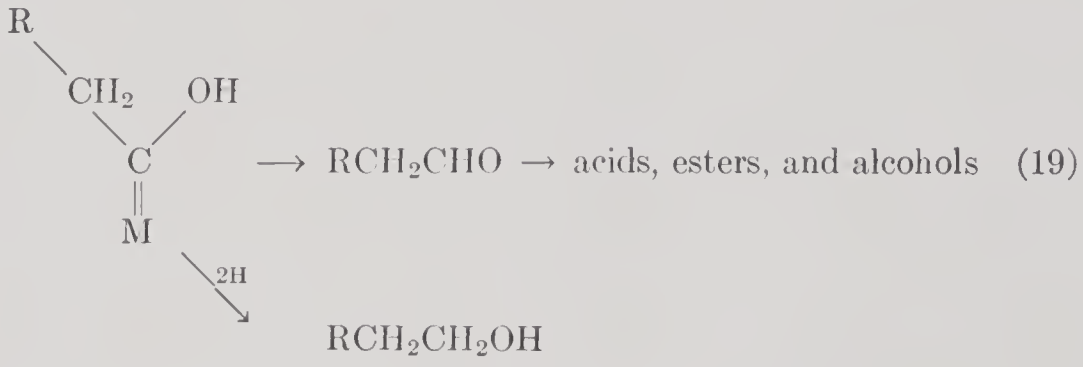
(α)



(18)

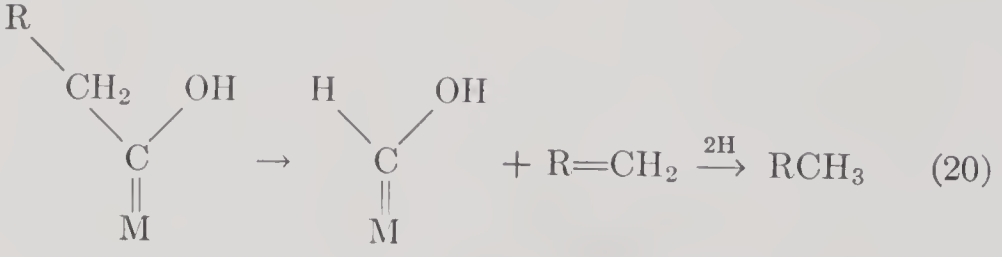
Chain ending

a.



(19)

b.



(20)

To summarize this section, we may conclude that the reaction mechanism of the Fischer-Tropsch synthesis is not clearly understood. The reaction is very selective, for the products are not those that have the greatest thermodynamic stability. The synthesis is a very slow catalytic reaction. The slow rate of synthesis and the selectivity of the catalyst may result from poisoning of the catalyst with some component of the synthesis, possibly carbon monoxide, since hydrocarbons are readily hydrocracked and hydrogenated by hydrogen in its absence. The role of carbide in the synthesis is still uncertain, but at least many parts of the detailed carbide theory of Craxford appear to be incorrect. The reaction mechanism probably involves the formation and condensation of groups containing oxygen.

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